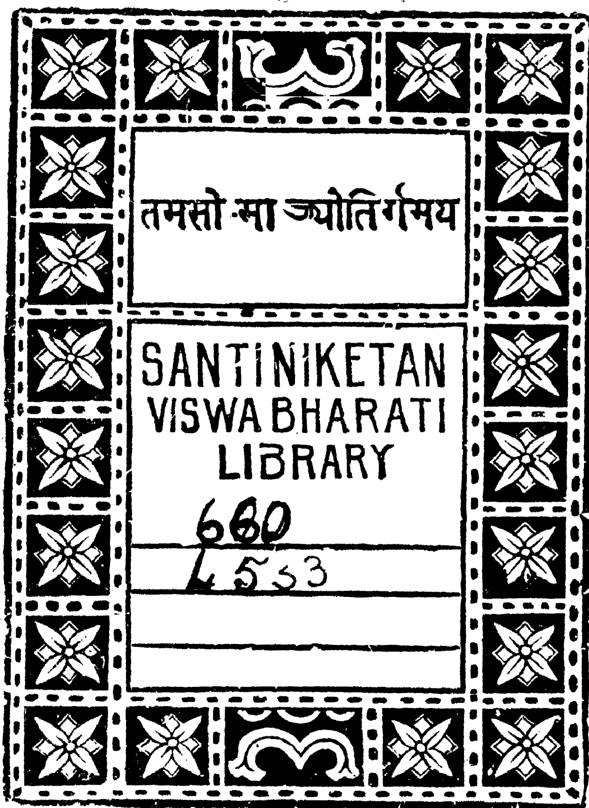
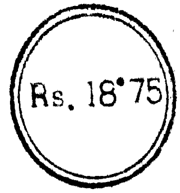


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CHEMISTRY

of

ENGINEERING MATERIALS

ROBERT B. LEIGHOU
Late Professor of Chemistry in the Carnegie
Institute of Technology

Rewritten by the following members of the Chemistry Faculty
of the Carnegie Institute of Technology

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Fourth Edition

ASIAN STUDENTS' EDITION

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PREFACE TO THE FOURTH EDITION

This Fourth Edition has been prepared to make available a modern version of a book which, over a period of twenty-five years, has been useful to students of science and engineering and to practicing engineers. The original purpose of Prof. Leighou has been retained, namely, that of providing information on the chemical properties of engineering materials so that these materials may be more intelligently selected and used.

As in the previous editions, it has been assumed that the reader, through formal course work, or by private study, has a knowledge of elementary general chemistry. Indeed, such knowledge is also necessary for the further study of various subjects through the periodical literature and books that are cited as references throughout the text. As a text, this book should be suitable for sophomore or junior engineering students. As a reference book, it should be useful to those practicing engineers whose formal training has not included the study of advanced courses in chemistry and metallurgy.

In the eleven years since the publication of the third edition, the improvement in the quality and increase in the variety of engineering materials has been amazing. This has made it necessary to rewrite all parts of the text to bring the description of old materials in line with modern developments in their manufacture and use, to delete descriptions of obsolete materials, and to add discussions of new materials. In general, emphasis has been placed on the properties of engineering materials rather than upon processes for their manufacture. In some cases, however, the process of manufacture has an important bearing upon the properties of the material and hence has been described.

Of the many changes in the text, the following deserve special mention: The analysis, treatment and behavior of water for steam generation has been discussed from the standpoint of physical chemical principles by an author of long practical experience in the field. The section on fuels has been expanded to include weight and volume relations in the combustion of fuels, the thermochemistry of combustion reactions, the principles of making heat and material

balances, and a discussion of modern high-octane motor fuels. Modern methods for the dewaxing and refining of lubricating oils and their improvement by addition agents are discussed.

The chapter on nonferrous alloys begins with an elementary but scientifically sound discussion of the phase rule and equilibrium diagrams for alloy systems. These principles are then used in the description of alloys and their properties. Steelmaking has been discussed from the standpoint of the influence of furnace, deoxidation, and teeming practice upon steel quality. In the chapter on alloys of iron, an attempt has been made to discuss the most recent information on the principles of heat-treating; to present casehardening, scaling, and protective atmospheres from the standpoint of physical chemical principles; and to give at least a brief account of the most important steels and irons and their engineering applications. The chapter on the technology of shaping metals and alloys, although brief, should give the reader a résumé of applications of the various shaping methods. The chapter on the corrosion of metals and alloys has been expanded to permit the presentation of the fundamental theory of electrochemical corrosion and its application to many practical cases. The fact that the nature of the environment is of an importance equal to that of the metal or alloy is stressed. This chapter may seem difficult to the reader, but it is believed that any engineer who masters its contents will be amply rewarded for his efforts. The growing importance of metallic and inorganic coatings has warranted a new chapter describing these materials.

Other new chapters are those devoted to abrasives, glass, and organic plastics. In the chapter on rubber, the principal types of synthetic rubbers (elastomers) are described. In the discussion of organic coatings, less emphasis has been placed on the production of raw materials and more space has been devoted to the newer types of coatings and to paint practice. The behavior of glues and adhesives has been explained on a basis of the principles of colloid chemistry, and the chapter on insulating materials includes a description of materials useful for heat insulation as well as those utilized as electrical insulators.

It should be mentioned that the statistical and economic data given on the various materials are for prewar years and, although they may be considered fairly normal peace-time figures, they do not, of course, represent the present-day, greatly expanded production of engineering materials.

It is a pleasure to acknowledge assistance from a great variety of sources. Our thanks are due to the following industrial firms, publishers, technical societies, laboratories, and individuals for information and for permission to reproduce figures and tables: Dr. E. P. Partridge; Koppers Company; American Institute of Mining and Metallurgical Engineers; Harbison-Walker Refractories Company; Baldwin Southwark Division of the Baldwin Locomotive Works; Prof. R. S. Williams; The Engineering Foundation; Dr. Samuel Epstein, Metals Research Laboratory of the Carnegie Institute of Technology; Prof. R. F. Mehl; Dr. Cyril Wells; Dr. E. C. Bain; Mr. Frank T. Sisco; Pitman Publishing Corporation; Dr. A. B. Kinzel; Mr. Walter Crafts; American Society for Metals; Prof. Joseph Newton; John Wiley and Sons, Inc.; Prof. G. E. Doan; and The Carnegie-Illinois Steel Corporation.

We are indebted to the following colleagues and friends with whom we have had critical discussions on various parts of the manuscript: Profs. R. F. Mehl, F. N. Rhines, and G. Derge, and Dr. Cyril Wells of the Metals Research Laboratory, Carnegie Institute of Technology; Dr. E. P. Partridge of the Hall Laboratories; and Dr. R. B. Mears and Mr. R. H. Brown of the Aluminum Research Laboratories.

Finally, the editor of this edition is glad to acknowledge the help of Janet McVicar Fugassi who prepared the index, and to thank the other members of the Carnegie Chemistry Faculty who have so willingly cooperated in this project by writing various chapters.

J. C. WARNER.

PITTSBURGH, PA.,

PREFACE TO THE THIRD EDITION

In the six years that have elapsed since the previous revision of this text, the new developments in the fields with which it deals have been unusually rapid, and a new revision has become necessary in order to bring the subject matter into conformity with the advances that have been made. The work of Bergius, Fischer, and others on the conversion of coal into oil by hydrogenation has changed the outlook with respect to the fuel situation. The development of the high-compression engine, with its demand for anti-knock gasoline, has caused a swinging from the liquid-phase to the vapor-phase methods of cracking petroleum intermediates. The commercial production of light, strong aluminum alloys, capable of hardening by heat-treatment, has made necessary the presentation of a new theory relating to the hardening of metals. With the placing of the Aston process on a commercial basis, an entirely new principle has been injected into the age-old method of manufacturing wrought iron. The introduction of a non-ferrous alloy, harder than the sapphire, for tool bits has proven to be of great importance in industries employing machine tools. The work of Evans and his collaborators has apparently solved the baffling problem of the passivity of metals. In revising the text, these developments and many similar ones have received attention.

In the chapter on non-ferrous metals, magnesium and cadmium have been added to the industrial group; and the metallurgical processes, properties, and uses of all the metals have been described more fully. Several new pages, including more photomicrographs and more thermal diagrams, have been added to the chapter on non-ferrous alloys. The presentation of the subject of iron corrosion has been greatly improved by a discussion of the effect of primary oxide films. The chapter on foundry sands has been entirely rewritten. A section on high early-strength cements has been added to Chapter XI. The cellulose nitrate lacquers and lubricating greases, both of which have gained in importance through the growth of the automobile industry, have been treated in a manner more in keeping with their present extensive use. Through improvement either in the

subject matter or in the method of presentation, most of the chapters have been modified to an important degree.

The author wishes to acknowledge his indebtedness to Liddell's "Handbook of Non-ferrous Metallurgy," Jeffries and Archer's "Science of Metals," Sutermeister's "Casein and Its Industrial Applications," and Klemgard's "Lubricating Greases." He wishes to thank all of those who have read portions of the revised manuscript, particularly Dr. Ulrich R. Evans for his helpful suggestions with respect to the treatment of the corrosion of metals. He desires also to thank the members of the Research Bureau of the Koppers Company for their help in revising the section on the by-product coking of coal. Finally, he ventures to express the hope that the new edition may be accorded a reception as kindly as was granted the two previous editions.

R. B. L.

PREFACE TO THE FIRST EDITION

The preparation of this text has been brought about by the pressure of circumstances. The author has for nine years been conducting a course in Chemistry of Materials in the College of Industries of the Carnegie Institute of Technology, and has been considerably inconvenienced by the lack of a text. The particular object of the work is to supply information concerning the chemical properties of the materials employed in the various courses in Building Construction and Equipment, and in Machinery Construction and Operation, so that these materials might be used more intelligently and, therefore, to a better advantage. Although there are many tests on Industrial Chemistry covering the methods by which these materials are manufactured, nothing has appeared emphasizing their properties from the standpoint of the user. This is, then, the special purpose of the present text. It would naturally be understood that it is not possible to divorce entirely the discussion of the properties of any material from the discussion of the methods of its manufacture, but the latter have not been emphasized or presented in detail.

In preparing the material, the aim has been to avoid complexity of treatment in so far as possible, without becoming superficial. Although the treatment is by no means exhaustive, it is sufficiently complete to enable the student to gain a reasonably thorough knowledge of the various materials. Some theories, such as those that account for corrosion, the hardening of cements, the effect of the heat-treatment of steels, the electrochemical action in primary and secondary cells, etc., have been introduced; and although the nature of the work has made a full consideration of them inadvisable, it is believed that they have been developed in sufficient detail to avoid inexactness.

A prior course in Elementary General Chemistry has been assumed; indeed, this is considered essential not only for the study of this text, but for the understanding of any literature dealing with these or similar subjects. No special effort has been made to avoid the use of technical terms. It is considered one of the purposes of the text to explain such terms, and render them sufficiently familiar

so that students whose training otherwise might be insufficient for the demand, may be encouraged to make use of reference works, scientific magazines, journals, and similar literature in which technical terms are commonly employed. In fact, the author feels that if the text accomplishes no other object than to point the way to such sources of knowledge, it will have performed a valuable service.

The references to literature, from which a considerable amount of the material of the text has been drawn, have been indicated in the footnotes and listed at the ends of the chapters in order that the student may have recourse to them to extend the study of the subject when this is desired. An effort has been made in all cases to acknowledge the source of information obtained from these writings, and if any such acknowledgment has been omitted, it has not been done designedly.

The author wishes to acknowledge his indebtedness to C. A. Coulter for his aid in preparing certain illustrations. Also, he wishes to thank the following publishers for permission to use illustrations: Charles Griffin and Company, Ltd., for photomicrographs from their treatise on Alloys by Gulliver and Law; Sauveur and Boylston for photomicrographs from Sauveur's "Metallography of Iron and Steel"; McGraw-Hill Book Company, Inc., for photomicrographs from Gardner's "Paint Technology and Tests"; and the following manufacturers for photographs and electrotypes: Harbison-Walker Refractories Company for photomicrographs and illustrations of metallurgical furnaces and coke ovens; Pratt and Lambert for photographs relating to varnish and varnish materials; The Edison Storage Battery Co. and the Electric Storage Battery Co. for electrotypes showing their products.

R. B. L.

PITTSBURGH, PA.,
January, 1917.

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CHEMISTRY OF ENGINEERING MATERIALS

CHAPTER I

WATER FOR STEAM GENERATION

By David S. McKinney, D.Sc.

Because of the intimate connection of steam with the development of power and because of its wide application in other ways, the whole subject of steam generation is of considerable importance. But, since the conversion of water from the liquid to the vapor phase is essentially such a simple process, the need for intelligent supervision in the development of steam from natural waters on an industrial scale is apt to be overlooked. The purpose of the present chapter is to discuss briefly the more important of the many real problems connected with the process. Since the difficulties that attend the successful operation of steam boilers are due in a large measure to the impurities in the waters available for use, these should be considered first.

Impurities in Natural Waters

In a chemical sense, all natural waters are to some degree impure. Even rain water, which is the purest form, is saturated with the atmospheric gases and contains solid matter, both organic and mineral, obtained by washing out soot and wind-raised dust from the air. In fact, the generally accepted theory now is that the production of rain depends upon the presence in the air of dust particles, which serve as nuclei about which the drops may form. All waters obtained from the earth, whether from the surface or lower depths, contain dissolved substances taken up from the rocks and soils with which they have been in contact. Water from very low levels, as from deeply bored wells, is likely to contain larger quantities of dissolved substances than surface water, because of

the great mass of rock through which it has percolated. In general, water from regions of granite, sandstone, and clay formations contains much less dissolved mineral matter than that from limestone regions. Further, water from rocky regions is purer than that from regions where the rock has been disintegrated to form soil, since rocks are generally less soluble than soils. Mountain waters are relatively pure because they usually come into contact with little soil. Besides the dissolved substances, water may carry a great deal of suspended matter, as silica, clay, and organic material. This is especially true of surface waters, such as those from rivers and other streams.

Hard Water[1]

Water that contains dissolved calcium, magnesium, iron, and aluminum compounds is known as "hard water." This term, which should be applied only to water containing these substances, is used loosely in popular language to describe acidulated water, or water containing any substance that prevents soap from lathering. Calcium, magnesium, iron, and aluminum ions react with ordinary soluble soaps to form insoluble, sticky soaps of these metals. The reaction of sodium stearate, a typical soluble soap, with calcium ion is as follows: $2Na(C_{18}H_{35}O_2) + Ca^{++} = Ca(C_{18}H_{35}O_2)_2 + 2Na^+$. The soluble soap will not form a lather until a sufficient quantity has been added to precipitate all the metal ions producing hardness. This is the basis of the well-known soap method for determining hardness. Although widely used, this test is not recommended except as an approximate field test. The most accurate method for ascertaining hardness is to calculate it from the calcium, magnesium, iron, and aluminum determinations. The total hardness as $CaCO_3$ in parts per million is fifty times the sum of the equivalents per million of Ca, Mg, Fe, and Al, since the equivalent weight of $CaCO_3$ is 50.

The amount of hardness equivalent to the sum of the carbonate and bicarbonate ions is called "carbonate hardness," and the amount of hardness in excess of this is called "noncarbonate hardness." This method of subdivision is preferable to the older way of dividing the hardness into "temporary" and "permanent" hardness since the latter method cannot be definitely interpreted in terms of the chemical species existing in the water. The "temporary" hardness

[1] "Standard Methods of Water Analysis," American Public Health Assoc. and American Water Works Assoc. (1936).

is that removed by boiling. The removal is due in part to decomposition of bicarbonates to form insoluble carbonates and in part to the increase in pH, resulting from the removal of carbon dioxide, which causes the precipitation of the less soluble basic salts and hydroxides. "Permanent" hardness is that which persists after boiling. It includes the carbonate hardness not removed by boiling and the major part of the noncarbonate hardness.

Water that has been in contact with limestone deposits is likely to have a high carbonate hardness. Calcium carbonate is only very slightly soluble in pure water, but in water containing carbon dioxide, the normal carbonate is converted into bicarbonate, which is much more soluble. $CaCO_3(s) + CO_2(g) + H_2O = Ca(HCO_3)_2$ or $CaCO_3(s) + CO_2(g) + H_2O = Ca^{++} + 2HCO_3^-$. The necessary carbon dioxide is produced by the decay of organic matter under the action of bacteria in the soil. Water from deposits of marl, a mixture of calcium carbonate and organic matter, contains much calcium bicarbonate.

Acidity of Mine Water

In streams fed by tributaries that carry drainage from mines or from refuse that has been removed from mines, the water may contain considerable free sulfuric acid. The acid is produced by the wet oxidation of such sulfides as marcasite or iron pyrite, FeS_2, as follows:



$$4FeS_2(s) + 15O_2 + 6H_2O = 4Fe(OH)SO_4(s) + 4H_2SO_4$$

Reports of Water Analyses[1]

Although the dissolved solids in the water may be sufficient to cause considerable trouble in a boiler, the actual amounts are small compared with the water itself. If the solids shown by analysis were reported in percentages, their true significance might not be apparent, because even in a so-called "bad" water, the total solids may be only 0.03 or 0.04 per cent. An analysis reported on this basis, would, therefore, show approximately 99.97 per cent of water, a percentage that might lead one to believe that the water is essentially pure. In order to overcome this difficulty and to avoid showing percentages in the third or fourth place of decimals, water analyses are generally reported in parts per million by weight (ppm).

[1] A.S.T.M. Standards, Supplement, Part III (1941), p. 247. Designation D596-41.

Some analyses are reported in grains per gallon, especially in British literature. One grain per U. S. gallon is 17.1 ppm, and one grain per British gallon is 14.3 ppm. Because of the greater ease in making calculations, the use of parts per million is preferred. If many calculations of water treatment are to be made, it will be found convenient to report water analyses in equivalents per million parts by weight (epm), since one equivalent of one substance will react with or replace one equivalent of any other substance. To convert parts per million to equivalents per million, divide the parts per million of the given substance by its equivalent weight.[1]

Hardness, alkalinity, and acidity of water are often reported in terms of the equivalent amount of calcium carbonate, found by multiplying the number of equivalents per million of the substance by 50, the equivalent weight of calcium carbonate.

In the older literature, it was customary to combine the positive ions (cations) with the negative ions (anions) in the water, and report the resulting combinations as salts existing in the water. Depending on the order in which the combinations were made, several reports, bearing little apparent resemblance to one another, might be made from the same water analysis. The modern theory of electrolytes tells us that all salts are completely dissociated into ions in dilute solutions. Hence hypothetical combinations give an entirely false impression of the chemical substances present in solution. Furthermore, practically all reactions occurring in the treatment of water are reactions between ions. We shall therefore use ionic reactions as much as possible and shall write molecular formulas only when the substance concerned is undissociated or appears in the reaction as a gaseous or solid phase.

A selected list of water analyses is given in Table 1. Sample 1 represents approximately the maximum total solids to be expected in a "fresh" water. High sodium and chloride indicate that this water has been contaminated with sea water (sample 6). Sample 2 represents one of the purest supplies to be found in the United States. Rain water in industrial areas will contain at least as much dissolved material as this sample. Sample 3 is a very hard water. It will be noted that the bicarbonate and sulfate are both high and

[1] An equivalent or equivalent weight, as used in this chapter, is the molecular or ionic weight divided by the valence of the reacting ion. For definition in oxidation-reduction reactions see p. 407. See also McCutcheon, Seltz, and Warner, "General Chemistry," Chap. XVI, D. Van Nostrand Company, Inc., New York (1939).

TABLE 1.—WATER ANALYSIS OF SOME TYPICAL SUPPLIES*

Sample no. and source	Total dissolved solids ppm	Loss on ignition ppm	Silica, SiO_2 ppm	Iron, Fe, present as Fe_2O_3 ppm	Calcium, Ca^{++} ppm	Magnesium, Mg^{++} ppm	Sodium and potassium ppm	Bicarbonate, HCO_3^- ppm	Sulfate SO_4^{--} ppm	Chloride Cl^- ppm	Nitrate NO_3^- ppm	Hardness as $CaCO_3$ ppm
1. Tampa, Fla.	1,273	80	22	0.48	113	33	275	176	92	548	2.8	418
2. Catskills, N. Y.	28	2.5	2.6	0.04	4.5	1.2	1.7	11	7.7	1.0	0.49	16
3. Bloomington, Ill.	969	....	16	0.14	203	74	16.7	504	404	8.0	0.0	811
4. Dayton, Ohio	434	17	10	0.09	92	34	9.6	339	84	9.6	13	369
5. Pittsburgh, Pa.	148	....	8.2	0.2	28	4.6	8.5	27	60	13	0.8	66
6. Sea water	34,300	....	2.4	0.2	407	1,270	10,800	137	2,640	19,000	0.9	6,250

* From *U. S. Geol. Survey, Water Supply Paper* 496 (1921) and Smithsonian Physical Tables.

that most of the dissolved solids may be accounted for by the hardness of the water. This hardness has probably been acquired by percolation through beds of limestone and gypsum. Sample 4 is a moderately hard water in which most of the hardness is of the carbonate variety characteristic of water from limestone districts. The nitrate content of this water is unusually high. Sample 5 is a low-hardness water characteristic of streams that are fed chiefly by surface drainage. Here the carbonate hardness is usually lower than the noncarbonate hardness.

It should be noted that the calcium content of fresh water is high relative to the magnesium content; in sea water the reverse is true. Fresh waters seldom contain very much alkali metals, or chlorides.

Waters containing less than 150 ppm of hardness are generally classed as "good," those containing from 150 to 350 ppm as "fair," and those exceeding 350 ppm as "bad."

The Purpose of Water Treatment

Water for steam generation is treated by both mechanical and chemical methods to prevent or minimize scale and corrosion. The mechanical methods used are distillation (evaporation) to remove dissolved solids and nonvolatile acids from the water and deaeration for the removal of corrosive gases such as oxygen, carbon dioxide, and hydrogen sulfide. Good evaporators, carefully operated, should produce a distillate containing less than 5 ppm dissolved solids. The guarantees of makers usually vary with the quality of the water but are seldom below this figure. The corrosive gases, oxygen and carbon dioxide, are removed by deaeration, either in ordinary open heaters which will reduce the oxygen to approximately 0.7 ppm or in specially designed deaerating heaters capable of reducing the oxygen to 0.05 ppm or less. Methods of chemical treatment will be discussed at length below.

The choice of a method of treatment is dictated by the character of the water, its intended use, and the relative economy of the various methods of treatment. A suitable method of treatment should, of course, remove from the water a large proportion of the hardness that causes scale and deposits in boilers and pipe lines. Also, the dissolved salts remaining after treatment should be sufficiently low so that deposits in superheaters and turbines (due to foaming and priming of the boiler) may be avoided by "blowing down" a reasonably small proportion of the boiler water.

Referring to Table 1, sample 2 is so pure that it cannot be materially improved by the ordinary chemical softening methods; sample 6 is so high in dissolved solids that it would be useless for steam generation even after softening. Sample 2 could be used directly in internally treated boilers and sample 6 would be purified by distillation. Sample 2, and perhaps sample 5, could be used without treatment other than adjustment of alkalinity in low-pressure boilers (less than 100 psi), but would probably cause serious trouble in high-pressure boilers, which tolerate very little scale. Evaporation is commonly used to produce the make-up requirements on ocean-going ships, and in central power stations where the make-up is low. It is also used in steam heating plants, in which the condensate is returned to the boilers, when the low-pressure steam from the evaporators can be discharged directly into the low-pressure steam lines.

Water Softening

The process of treating water to remove the hardness-producing ions, calcium, magnesium, and sometimes iron and aluminum, is called softening and the resultant water, containing very little of these ions, is known as soft water. The two best known processes for accomplishing this are the lime-soda and the zeolite or base-exchange process. These, with their modifications, will now be described. The results to be expected on treating water 4 (Dayton, Ohio) of Table 1 are given in Table 2.

The Cold Lime-soda Process

In both the cold and the hot lime-soda processes, magnesium ion is removed as the hydroxide and calcium ion as the carbonate by means of lime, CaO, and soda ash, Na_2CO_3. A coagulant must often be employed in the cold lime-soda process, since the precipitates produced are very finely divided; therefore, they neither settle rapidly, nor can they be efficiently removed by filtration. Aluminum sulfate, alum, sodium aluminate, and ferrous sulfate are used for this purpose. All these substances produce flocculent, gelatinous precipitates that entrap the suspended matter and finely divided precipitates, settle rapidly, and are easily retained on the filters.

The older cold lime-soda softeners were usually of the batch or intermittent type. Water and the necessary chemicals are added to a large tank supplied with low-speed agitators. After thorough

TABLE 2.—EXPECTED RESULTS OF TREATMENT OF WATER 4, TABLE 1, BY VARIOUS METHODS

	Untreated		Cold lime-soda process		Hot lime-soda process		Sodium zeolite process		Carbonaceous (acid) zeolite process	
	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm
Hydroxide, OH^-	0	0.00	6.8	0.40	1.4	0.08	0	0.00	0	0.00
Carbonate, CO_3^{--}	0	0.00	21	0.70	21	0.70	0	0.00	0	0.00
Bicarbonate, HCO_3^-	339	5.56	0	0.00	0	0.00	339	5.56	0	0.00
Sulphate, SO_4^{--}	84	1.75	84	1.75	84	1.75	84	1.75	84	1.75
Chloride, Cl^-	9.6	0.27	9.6	0.27	9.6	0.27	9.6	0.27	9.6	0.27
Nitrate, NO_3^-	13	0.21	13	0.21	13	0.21	13	0.21	13	0.21
Silica, SiO_2	10	0.33	5*	0.17	5*	0.17	10	0.33	10	0.33
Iron, Fe^{+++}	0.06									
Calcium, Ca^{++}	92	4.60	6	0.30	6	0.30	2	0.10	2	0.10
Magnesium, Mg^{++}	34	2.80	1	0.08	1	0.08	0.5	0.04	0.5	0.04
Sodium, Na^+ calculated	9	0.39	68	2.95	60	2.63	176	7.65	1.8	0.08
Hydrogen, H^+									2	2.01
Hardness, $CaCO_3$	369	7.38	19	0.38	19	0.38	7†	0.14	7†	0.14

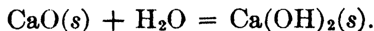
* Expect some SiO_2 removal because of high ratio of Mg to SiO_2 in raw water; exact extent unpredictable.

† Better hardness removal is possible with very careful operation.

mixing the agitators are stopped and the sludge allowed to settle. Water is then drawn off through sand filters as needed. To make the process continuous, two agitator tanks are provided so that, while one tank is being treated, the other supplies softened water to the system. Several filters are also provided so that one may be cleaned while filtration proceeds in the others. Although sand is generally used in the filters, this material is sometimes replaced by sized anthracite coal, coke, or dense iron ore. The precipitated sludge is not removed from the treating tanks at the end of each cycle, since it aids materially in the coagulation of the next batch of water. The amount of coagulant required is found by trial.

The majority of cold-process softeners being built today are of the continuous type. The two agitator tanks of the cold-batch process are replaced by a two-chambered reaction tank. The water and treating chemicals are introduced into the smaller chamber, which is provided with agitators to secure thorough mixing. The water then flows upward through the second and larger chamber, of rapidly increasing cross section. Owing to the decreasing velocity of the water as it flows through the second chamber, a zone is reached where the rate of settling of the sludge is equal to the rate of upward flow of water and above which the water is practically free of sludge. The clarified water is drawn off the top of the second chamber and is filtered as in the batch process. Sludge is continuously discharged from the sludge zone, a portion of it being recirculated to the first chamber to secure better coagulation, the remainder being discarded. Owing to the decrease in viscosity of the water with rising temperature and the consequent increase in the sludge settling rate, the capacity of the softener may be twice as great in summer as in winter.[1]

The lime is usually slaked and added to the water as a suspension known as "milk of lime." The slacking reaction is



$$CaO(s) + H_2O = Ca(OH)_2(s).$$

Sufficient lime must be added to

1. Neutralize the free mineral acid, if present.

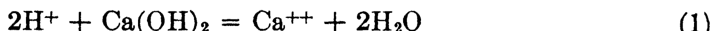
2. Precipitate the coagulant, if of an acid nature such as aluminum sulfate, alum, or ferrous sulfate.

3. Convert CO_2 and HCO_3^- to CO_3^{--} ion.

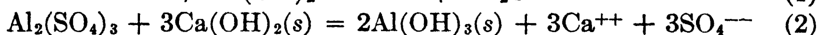
4. Precipitate Mg^{++} as the hydroxide.

[1] SPAULDING, *Water Works & Sewerage*, **85**, 153 (1938).

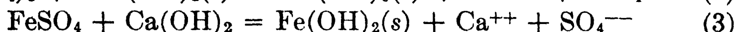
The reactions[1] in the order indicated above are



$$2H^+ + Ca(OH)_2 = Ca^{++} + 2H_2O \qquad (1)$$



$$Al_2(SO_4)_3 + 3Ca(OH)_2(s) = 2Al(OH)_3(s) + 3Ca^{++} + 3SO_4^{--} \qquad (2)$$

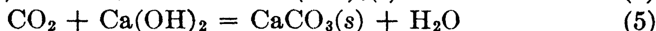


$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2(s) + Ca^{++} + SO_4^{--} \qquad (3)$$

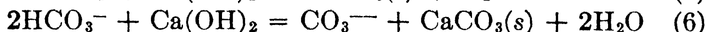
The ferrous hydroxide formed in reaction (3) is rapidly oxidized to ferric hydroxide by oxygen dissolved in the water.



$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3(s) \qquad (4)$$

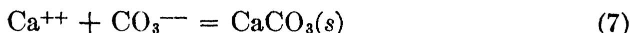


$$CO_2 + Ca(OH)_2 = CaCO_3(s) + H_2O \qquad (5)$$



$$2HCO_3^- + Ca(OH)_2 = CO_3^{--} + CaCO_3(s) + 2H_2O \qquad (6)$$

The carbonate ion formed in reaction (6) precipitates calcium ion already in the water.

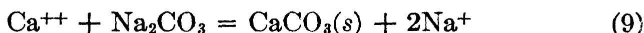


$$Ca^{++} + CO_3^{--} = CaCO_3(s) \qquad (7)$$



$$Mg^{++} + Ca(OH)_2 = Mg(OH)_2(s) + Ca^{++} \qquad (8)$$

Sufficient soda ash is then added to precipitate that part of the calcium originally present which is not removed by reaction (7), plus that introduced by the lime treatment [Reactions (1), (2), or (3) and (8)].



$$Ca^{++} + Na_2CO_3 = CaCO_3(s) + 2Na^+ \qquad (9)$$

If sodium aluminate is used as coagulant, no lime is required for its precipitation, and the lime requirement is diminished by an amount equivalent to the hydroxyl ion formed on hydrolysis of the sodium aluminate.



$$NaAlO_2 + 2H_2O = Na^+ + OH^- + Al(OH)_3(s) \qquad (10)$$

From the foregoing equations we may formulate simple rules for calculating the lime and soda ash requirements as follows:

1. When an acid coagulant such as alum or ferrous sulfate is used, the lime requirement, in equivalents, is the sum of the equivalents of mineral acids, carbon dioxide, bicarbonate ion, and magnesium ion in the water, plus the equivalents of coagulant added [Reactions (1), (5), (6), (8), and (2) or (3) respectively]. The soda ash requirement, in equivalents, is the sum of the equivalents of mineral acids, calcium ion, and magnesium ion in the water plus the equivalents of acid coagulant (if used) less the equivalents of bicarbonate ion. [Reactions (1), (9), (8), (2) or (3), (6), and (7).]

[1] The symbol (*s*) after a formula indicates that the compound is a solid, frequently formed as a precipitate.

2. When an alkaline coagulant, such as sodium aluminate, is used, the lime requirement in equivalents is the sum of the equivalents of mineral acids, carbon dioxide, bicarbonate ion, and magnesium ion in the water, less the equivalents of base formed by hydrolysis of the sodium aluminate. [Reactions (1), (5), (6), (8), and (10), respectively.] The soda ash requirement, in equivalents, is the sum of the equivalents of mineral acids, calcium ion, and magnesium ion less the equivalents of bicarbonate ion in the water and of hydroxyl ion formed by the sodium aluminate. [Reactions (1), (9), (8), (6), and (10).] These rules do not include excess reagents that may be added.

The use of the rules is illustrated in the following example based upon the analysis of water 4, Table 1, to secure the treated water of Table 2 by the cold lime-soda process. To make the example more complete, we shall assume that 14 ppm of $FeSO_4 \cdot 7H_2O$ is used as coagulant and that the water contained 30 ppm of free CO_2.

Analysis	Untreated water		CaO required epm	Na_2CO_3 required epm
	ppm	epm		
CO_2	30	1.36	1.36	
HCO_3^-	339	5.56	5.56	−5.56
Ca^{++}	92	4.60	....	+4.60
Mg^{++}	34	2.80	2.80	+2.80
$FeSO_4 \cdot 7H_2O$	14	0.10	0.10	+0.10
No excess reagent, total	...	....	9.82	1.94

In addition, the following excess of reagents is required to produce treated water containing concentrations of OH^- and CO_3^{--} indicated below.

Analysis	Treated water		Excess CaO required epm	Excess Na_2CO_3 required epm
	ppm	epm		
OH^-	6.8	0.40	0.40	0.40
CO_3^{--}	21.	0.70	.....	0.70
Including excess reagent, total	....	....	10.22	3.04

Weights of pure reagents required per million pounds of water treated:

$$FeSO_4 \cdot 7H_2O = 14 \text{ lb.}$$
$$CaO = 10.22 \times 28.04 = 287 \text{ lb.}$$
$$Na_2CO_3 = 3.04 \times 53 = 161 \text{ lb.}$$

It must be remembered that both calcium carbonate and magnesium hydroxide are soluble in water to a small but measurable extent. This solubility can be decreased by the use of excess reagents, in accordance with the solubility product principle, which states that, *at a given temperature, when a difficultly soluble compound is in equilibrium with its saturated solution, the product of the molal concentrations of its ions, each raised to the power which is the number of ions formed by the dissociation of one molecule of the compound, is equal to a constant. This constant is denoted by the letter L and is called the solubility product constant of the compound in question.* We would then write, for calcium carbonate: $L_{CaCO_3} = [Ca^{++}][CO_3^{--}]$, and for magnesium hydroxide: $L_{Mg(OH)_2} = [Mg^{++}][OH^-]^2$, where the brackets indicate concentrations in moles per liter. Considering the above equations, it is evident that an excess of sodium carbonate will decrease the residual calcium ion in the water and an excess of hydroxyl ion, produced by the use of excess lime, will reduce the residual magnesium. The excess treatment is usually adjusted to produce a softened water containing a minimum of 0.4 epm of hydroxyl ion and 0.7 epm of carbonate ion. The residual hardness of the treated water is of the order of 15 ppm, expressed as calcium carbonate. In calculating the weights of commercial chemicals, account must also be taken of the impurities that they contain. Advantage is taken also of the use of excess reagents in initiating the formation of the calcium carbonate and magnesium hydroxide precipitates in the batch process by adding the whole requirement of lime and soda ash to the treating tanks before they are filled with the water to be treated, agitation being started as soon as the paddles are covered.

Slight variations of the lime-soda process are sometimes used. For example, the lime may be partly replaced by sodium hydroxide. This is of no advantage in the batch process since sodium hydroxide can be prepared from lime and soda ash.



$$Ca(OH)_2 + Na_2CO_3 = 2NaOH + CaCO_3(s)$$

Some success has been reported in the removal of silica by the use of sodium aluminate with an approximately equivalent amount of magnesium sulfate, the resulting mixture of $Al(OH)_3$

and $Mg(OH)_2$ being especially effective in coagulating silica, which exists in most waters principally as a colloidal suspension. The removal of silica is usually difficult and expensive.

Barium carbonate and barium hydroxide have been occasionally substituted for the corresponding sodium salts to remove sulfates.



$$Ba^{++} + SO_4^{--} = BaSO_4(s)$$

They are seldom used today because of their relatively high cost and because soluble barium salts are poisonous.

The Hot Lime-soda Process

At ordinary temperatures, two to three hours are required for the completion of crystallization and coagulation in the cold lime-soda process, whereas, if the water is heated to near the boiling point, the reactions are essentially complete in approximately 15 min. It is apparent from this fact that a hot-process softener will be of considerably smaller size than a cold-process softener of equal capacity. The increase in temperature also reduces the viscosity of the water, allowing the use of smaller filters. The precipitated sludges usually settle so rapidly that a coagulant is not required. Where space is limited or sufficiently expensive to outweigh the additional cost of the apparatus, the hot-process softener would be selected in preference to the cold process. The hot-process softener is nearly always of the continuous type. The water is heated to the boiling point in an open deaerating heater. This removes the dissolved gases, including carbon dioxide, and, if the water contains appreciable carbonate hardness, accomplishes some softening due to the decomposition of bicarbonate ion as follows:[1]



$$Ca^{++} + 2HCO_3^{-} = H_2O + CaCO_3(s) + CO_2(g)$$

The water then passes into a closed tank provided with an agitator, where the additional chemicals required to complete the softening are added. The water is then filtered. The remaining reactions are identical with those given for the cold-process softener. The lime required for hot-process treatment is less than for the cold process since a coagulant is seldom used and because of the removal of carbon dioxide and the decomposition of bicarbonate ion in the deaerating heater. The treatment is usually adjusted to produce a softened water containing practically no hydroxyl ion and a mini-

[1] The symbol (g) after a formula indicates that the compound is in the gaseous state.

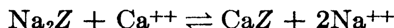
mum of 0.7 epm of carbonate ion. The continuous hot process requires careful control especially if the water supply is of rapidly varying composition. Any change in the water composition should be followed immediately by a proper adjustment of the chemical feed.

Since the solubility of calcium carbonate and magnesium hydroxide increases with temperature, the residual hardness (30 to 50 ppm as $CaCO_3$) after hot-process softening may be somewhat higher than in the cold process.

By using trisodium phosphate and sodium hydroxide in the hot-process softener, the residual hardness may be reduced below that obtainable by the use of lime and soda ash. However, the chemical cost is higher.

The Zeolite or Base-exchange Process

The zeolite process depends upon the ability of the zeolite minerals, complex sodium aluminum silicates, to exchange sodium ions for calcium and magnesium ions in the water. For calcium ion, the reaction is



$$Na_2Z + Ca^{++} \rightleftharpoons CaZ + 2Na^{++}$$

where Z stands for the complex aluminum silicate part of the molecule. Since this reaction is easily reversible, the zeolite will not soften waters containing large amounts of sodium. This reversibility is utilized in regenerating the spent zeolite with sodium chloride solution. Both natural and artificial zeolites are used, the former being the more durable, the latter having higher capacities per unit weight of zeolite. The artificial zeolite is made by fusing together feldspar, china clay, and soda ash; the resulting glass is cooled and crushed. If the water supply contains no suspended matter or free acid, it is merely allowed to flow through a bed of zeolite contained in a suitable tank. When the zeolite is exhausted, it is regenerated by flowing a strong solution of sodium chloride through the zeolite bed. This reverses the softening reaction given above, converting the exhausted calcium zeolite into the active sodium zeolite. The brine solution, now containing the calcium and magnesium removed from the water during the softening cycle, is washed out of the zeolite with fresh water and discarded. The salt requirement is approximately three times the theoretical value, owing to the necessity of maintaining a large excess of sodium ion in the regenerating brine.

When the water supply is clear, the zeolite system is commonly used without other treatment to soften water for laundries, small heating plants, municipal water supplies, and homes. Under these conditions the system can be adequately controlled by the simple soap test for hardness. Municipal water-softening plants are usually operated to leave approximately 50 ppm of hardness in the softened water by allowing a portion of the hard water to by-pass the softener. This hardness produces some deposit in the distribution lines, decreasing the rate of corrosion.

If the water supply is turbid, the suspended matter must be removed by coagulation and filtration before the water is admitted to the zeolite. Pretreatment is also required if the water is acid or very alkaline or if it contains appreciable amounts of iron and manganese.

Since the zeolite sand merely replaces calcium and magnesium with sodium ion, the bicarbonate ion and free carbon dioxide are not altered. The resulting very soft water is corrosive since it contains no material capable of producing a protective film on the metal of the pipe line. In high-pressure boiler systems the free carbon dioxide and a portion of that present as bicarbonate ion are liberated in the feed-water heaters. The remainder is liberated in the boilers.



$$HCO_3^- = CO_2(g) + OH^-$$

The resulting steam, when condensed, dissolves the liberated carbon dioxide. Since carbon dioxide is a weak acid, the resulting condensate may be very corrosive if the carbon dioxide content is high. Also the reaction above indicates that an equivalent of hydroxyl ion is formed in the boiler for each equivalent of bicarbonate ion decomposed. This results in a very alkaline boiler water which may require excessive blowdown to prevent foaming. For these reasons, the simple zeolite is seldom used for boiler feed-water treatment when the water to be treated is high in carbonate hardness.

Various schemes have been devised for supplementary treatment to remove the offending carbon dioxide and bicarbonate ion. The chemical control required by these more complicated systems of treatment is comparable to that required by the hot lime-soda process, but the hardness remaining in the zeolited water is considerably less than in the case of the lime-soda softened water.

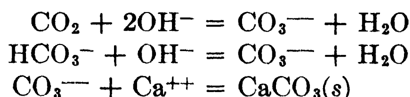
In some installations the zeolite-softened water is treated with sulfuric acid.



$$2HCO_3^- + H_2SO_4 = 2CO_2(g) + 2H_2O + SO_4^{--}$$

The bulk of the carbon dioxide is removed by aeration of the water, followed by deaeration to remove the remaining carbon dioxide and oxygen. Care must be taken to avoid an excess of sulfuric acid.

In other installations, the water is pretreated with lime or sodium hydroxide, combined with a coagulant, and filtered. This pretreatment is used when the water is acid or contains appreciable quantities of iron and manganese. The carbon dioxide and bicarbonate ion are removed as calcium carbonate in accordance with the following equations:



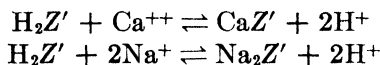
$$CO_2 + 2OH^- = CO_3^{--} + H_2O$$
$$HCO_3^- + OH^- = CO_3^{--} + H_2O$$
$$CO_3^{--} + Ca^{++} = CaCO_3(s)$$

The filtered water is then passed through zeolite sand which removes the remaining noncarbonate hardness. The reactions must be complete before filtration of the water, for if calcium carbonate precipitates after filtration, the zeolite grains may become coated. This stops the softening process and may require acid treatment of the zeolite before it can be regenerated. Afterprecipitation on the zeolite grains may be prevented by the "threshold treatment" described on page 31. This method of treatment is chemically equivalent to the lime-soda process, but owing to the high efficiency of the zeolite in removing hardness, the resulting water is softer than that produced in the lime-soda process, and also is lower in alkalinity since no excess lime or sodium hydroxide is required to secure efficient hardness removal. The lime or caustic soda treatment is adjusted to produce a pH (page 23) of about 8. The resulting water is considerably less corrosive than that produced by the simple zeolite method or by the zeolite followed by acid treatment.

Counterbalancing these advantages, the equipment is relatively expensive and requires careful control. When used on waters with high carbonate hardness, both this method and the lime-soda method result in a desirable decrease in the dissolved solids remaining in the treated waters, since the carbon dioxide and bicarbonate ion are precipitated as insoluble calcium carbonate. In the simple zeolite method, a slight increase in solids results since calcium, equivalent weight 20, and magnesium, equivalent weight 12, are replaced by sodium, equivalent weight 23.

Carbonaceous Zeolites[1]

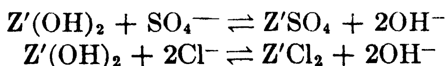
Several insoluble organic substances have come into use that have the property of exchanging ions in the same manner as do the zeolite minerals. For this reason they are known as carbonaceous zeolites. Although they may be used as ordinary zeolites, their principal advantage lies in the fact that they may be used for softening waters, such as acid mine waters, which will destroy the silicious zeolites, or for exchange reactions involving ions other than sodium. One type of carbonaceous zeolite is made by treating organic substances with fuming sulfuric acid or chlorosulfonic acid. These substances are regenerated with 0.5 to 4 per cent sulfuric acid and will replace practically all metallic ions in the water with hydrogen ion.



$$H_2Z' + Ca^{++} \rightleftharpoons CaZ' + 2H^+$$
$$H_2Z' + 2Na^+ \rightleftharpoons Na_2Z' + 2H^+$$

where Z' indicates the complex organic part of the carbonaceous zeolite. The equipment used must be acid proof. Wood or rubber-lined steel tanks and hard rubber or rubber-lined steel piping have been used. Chemical stoneware also could be used.

Synthetic phenolic resins have been prepared, some of which function as hydrogen ion (cation or positive ion) exchangers, others as anion (or negative ion) exchangers. These latter substances are regenerated with sodium hydroxide or sodium carbonate. They remove sulfate ion very efficiently, chloride ion somewhat less efficiently, and have little effect on bicarbonate ion. If regenerated with sodium hydroxide, the reactions are as follows:

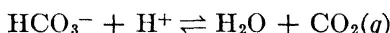


$$Z'(OH)_2 + SO_4^{--} \rightleftharpoons Z'SO_4 + 2OH^-$$
$$Z'(OH)_2 + 2Cl^- \rightleftharpoons Z'Cl_2 + 2OH^-$$

The cation exchangers are used in combination with ordinary zeolites to avoid sulfuric acid treatment for removal of bicarbonate. A portion of the water is softened by the ordinary mineral zeolite, another portion by the carbonaceous zeolite. The carbonaceous zeolite removes practically all the metallic ions, replacing them with hydrogen ions. The rates of flow through the two zeolites are so adjusted that the hydrogen ion introduced by the carbonaceous

[1] Tiger, *Trans.* A.S.M.E. **60**, 315 (1938). Bird, *Proc.* A.S.T.M. (1938), Part 2, 631.

zeolite will convert nearly all of the bicarbonate ion in the water from the mineral zeolite to carbon dioxide.



$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2(g)$$

The carbon dioxide is then removed by aeration followed by deaeration. The total solids remaining in water treated in this way are less than if sulfuric acid is used to remove bicarbonate.

The organic cation exchangers are also used, in combination with anion exchangers, to produce water approaching distilled water in purity. The water is passed first through the cation exchanger, where practically all the metallic ions are replaced by hydrogen ion, then through the anion exchanger where sulfate and chloride ion are replaced by hydroxyl ion. The hydroxyl ion neutralizes a portion of the hydrogen ion, resulting in a water that contains free carbon dioxide with traces of salts. The carbon dioxide is then removed by aeration and deaeration. Little operating information is as yet available on these materials.

Boiler Scale and Deposits

When water is converted into steam, both the suspended and the dissolved materials may be deposited within the boiler. If these substances form adherent coatings on the metal surfaces, they are called scales; if not, they are known as sludges. The suspended matter may be coagulated owing to the increase in temperature within the boiler, or it may be entrapped by crystallizing soluble material. In order that soluble material may be deposited, the solubility product for the solid substance must be exceeded. This may be caused by the normal increase in concentration that occurs due to evaporation within the boiler, to a decrease of the solubility of the dissolved substance, or to reactions that produce insoluble substances from others previously soluble. The importance of the first cause will be at once recognized from the fact that modern high-pressure boilers may evaporate an amount of steam equal to the water they contain in as short a time as 15 min. Thus, in a short time, even a well-softened water will be concentrated to the point where solid materials start to deposit. If the solubility of the dissolved substance decreases with temperature, as is the case with calcium sulfate (Fig. 1), it will deposit as an adherent scale on the heating surfaces of the boiler, and as sludges in the cooler regions. If the solubility increases with temperature, the material will form sludges in the hotter regions and scale on cooling surfaces. These

principles were first enunciated by R. E. Hall,[1] who was also the first to make use of the solubility product in the treatment of boiler waters. Hall's ideas were confirmed experimentally by Partridge and White[2] for the case of calcium sulfate. The latter authors observed the formation of steam bubbles at a heated surface in a solution

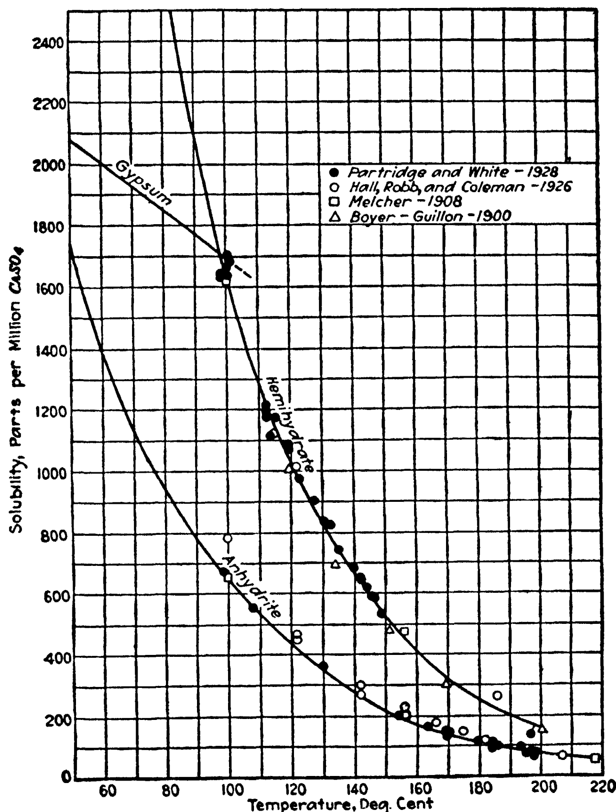


FIG. 1.—Solubility of calcium sulfate. (*Partridge and White, Trans. Am. Soc. Mech. Eng.*, **51**, 883, 1929.)

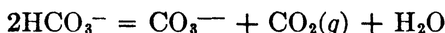
of calcium sulfate. A ring of tiny crystals of calcium sulfate was seen to form on the metal surface near the periphery of the steam bubble. These crystals do not redissolve when the steam bubble escapes, since the solution is already saturated. Repetition of this process gradually forms a solid layer of scale. An alternate explana-

[1] HALL, *et al.*, *Ind. Eng. Chem.*, **17**, 283 (1925); **21**, 826 (1929). *Carnegie Inst. Tech. Bull.* 24 (1927).

[2] PARTRIDGE and WHITE, *Ind. Eng. Chem.*, **21**, 834 (1939).

tion, which does not require that the solubility of the scale-forming substance decrease with temperature, is as follows. When a steam bubble forms on a metal surface, a film of water is left, which evaporates leaving a layer of dried salts. The bubble then escapes and the surface is again wetted but, if a new bubble forms before the salts previously deposited have time to redissolve, a layer of scale may be formed.

The formation of calcium carbonate due to the decomposition of bicarbonate ion into carbonate ion and carbon dioxide gas is an example of the formation of a deposit due to chemical reaction. At elevated temperatures, bicarbonate ion decomposes as follows:



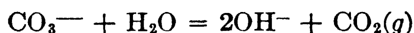
$$2HCO_3^- = CO_3^{--} + CO_2(g) + H_2O$$

The carbon dioxide escapes with the steam. Carbonate ion combines with calcium ion to form calcium carbonate.



$$Ca^{++} + CO_3^{--} = CaCO_3(s)$$

This reaction may take place in low-pressure boilers (less than 100 psi). In high-pressure boilers the partial pressure of CO_2 in the steam is usually lower than that produced by a saturated solution of calcium carbonate. Under these conditions carbonate ion decomposes,



$$CO_3^{--} + H_2O = 2OH^- + CO_2(g)$$

and cannot reach a value sufficiently high to precipitate calcium carbonate.

The most troublesome scales consist of calcium sulfate or calcium and magnesium silicates. Calcium and magnesium hydroxides and calcium carbonate are less frequently major constituents of scales. These substances, together with iron and aluminum oxides, are often entrapped in the sulfate and silicate scales during their formation. In very high-pressure boilers, sodium aluminum silicate scales have been found that resemble the zeolite minerals. These occur in regions of excessive local evaporation.

Effect of Deposits within the Boiler

The deposition of scale on the heating surfaces constitutes a serious hazard in the operation of a boiler. All scales are good heat insulators. Hence the formation of scale on the tubes or other heated surfaces may insulate the metal so well that it becomes overheated and is not strong enough to withstand the boiler pressure.

"Bagging" of the tubes then occurs, and the scale cracks, admitting water to the overheated surface. This cools the surface and stops the swelling of the tube until a new layer of scale forms and the process is repeated. Eventually the tube bursts. In addition to the loss of strength due to overheating, rapid reaction between water and iron occurs at high temperatures, causing additional thinning of the tube wall.



$$3Fe + 4H_2O = Fe_3O_4(s) + 4H_2(g)$$

In modern boilers, the increase in the rate of heat transfer through the tubes exposed to the fire, due to increased furnace temperatures and the increase in operating pressure with consequent increase of the water temperature within the boiler, makes the problem of scale formation a very serious one. Failure[1] has been known to occur in a 1,300 psi boiler when the scale thickness was only $\frac{1}{32}$ in. When scale formation is not prevented, frequent and expensive outages of the boiler for cleaning will be required to ensure that the scale does not reach a dangerous thickness. Boiler tube failures may also be due to steam blanketing caused by inadequate provision for the escape of steam from the generating tubes or by excessively high rates of heat transfer. Correction of the boiler design is necessary to eliminate this type of failure.

Excessive sludge accumulation may cause trouble within a boiler by settling in regions of poor water circulation or by plugging openings such as gauge-glass connections. When scale forms in a sludge-laden water, considerable quantities of the sludge may be entrapped within the scale.

Internal Treatment of Boilers to Prevent Scale Formation

From the foregoing discussion it is evident that the most objectionable deposits in boilers are caused by those substances whose solubilities decrease with rising temperature, producing adherent scales on the heat-absorbing surfaces. If the boiler water can be treated so that one of the constituent elements of the scale will be precipitated as a compound whose solubility increases with rising temperature, the offending element will deposit as a sludge that can be removed by blowing down, and scale formation on the heating surface will be prevented. To prevent the formation of calcium sulfate scale, calcium may be precipitated as calcium carbonate or as calcium phosphate, both of which deposit as sludges. At

[1] Anderson, *Engineer*, November, 1927, p. 605.

pressures below 150 psi, treatment with sodium carbonate to produce calcium carbonate has been successful. Above this pressure the carbonate ion decomposes so rapidly, producing carbon dioxide and hydroxyl ion, that it is necessary to use one of the sodium phosphates, precipitating the calcium as tricalcium phosphate. We shall first consider the conditions for the carbonate treatment. If the boiler water is saturated with both $CaSO_4$ and $CaCO_3$, the solubility products of both salts must be satisfied:

$$L_{CaCO_3} = [Ca^{++}] \cdot [CO_3^{--}] \qquad \text{and} \qquad L_{CaSO_4} = [Ca^{++}] \cdot [SO_4^{--}]$$

The bracketed quantities indicate concentrations in moles per liter. Since $[Ca^{++}]$ is identical in these expressions, we may write

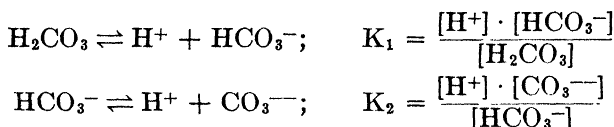
$$\frac{L_{CaCO_3}}{L_{CaSO_4}} = \frac{[Ca^{++}] \cdot [CO_3^{--}]}{[Ca^{++}] \cdot [SO_4^{--}]} = \frac{[CO_3^{--}]}{[SO_4^{--}]}$$

If the ratio $[CO_3^{--}]/[SO_4^{--}]$ is maintained greater than $[L_{CaCO_3}]/[L_{CaSO_4}]$ by the addition of sodium carbonate, the water is saturated with calcium carbonate, but not with calcium sulfate. Hence calcium sulfate cannot deposit and no scale will form. In order to utilize the sodium carbonate efficiently, it is necessary, since carbon dioxide is a very weak acid, to maintain the hydroxyl-ion concentration sufficiently high so that most of the carbon dioxide is present as carbonate ion. The hydroxyl- and hydrogen-ion concentrations are related by the dissociation constant of water.



$$H_2O \rightleftharpoons H^+ + OH^-; \qquad K_W = [H^+] \cdot [OH^-]$$

Hence a high concentration of hydroxyl ion requires that the hydrogen-ion concentration be correspondingly low, to satisfy this equation. The relations between the hydrogen-ion concentration and the remaining ions of carbonic acid are given by the dissociation constants of carbonic acid.



$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \qquad K_1 = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}; \qquad K_2 = \frac{[H^+] \cdot [CO_3^{--}]}{[HCO_3^-]}$$

The second of these equations shows that, as the hydrogen-ion concentration is decreased, the ratio $[CO_3^{--}]/[HCO_3^-]$ must increase correspondingly, *i.e.*, the fraction of the total CO_2 present as CO_3^{--} must increase. The relations existing at 25°C. are given in Table 3 from which it is evident that the hydroxyl-ion concentration must

TABLE 3.—DISTRIBUTION OF IONS IN WATER AT VARIOUS pH VALUES, 25°C.*

pH	Concentration moles per liter		Percentage of total moles of CO_2, present as			Percentage of total moles of H_3PO_4, present as			
	H^+	OH^-	H_2CO_3	HCO_3^-	CO_3^{--}	H_3PO_4	$H_2PO_4^-$	HPO_4^{--}	PO_4^{---}
4	10^{-4}	10^{-10}	99.6	0.4	....	1.3	98.6	0.1	
5	10^{-5}	10^{-9}	95.9	4.1	....	0.1	99.3	0.6	
6	10^{-6}	10^{-8}	69.9	30.1	....	...	94.2	5.8	
7	10^{-7}	10^{-7}	18.8	81.1	0.1	...	61.7	38.3	
8	10^{-8}	10^{-6}	2.3	97.2	0.5	...	13.9	86.1	
9	10^{-9}	10^{-5}	0.2	95.3	4.5	...	1.6	98.3	0.1
10	10^{-10}	10^{-4}	....	68.0	32.0	...	0.2	98.8	1.0
11	10^{-11}	10^{-3}	....	17.5	82.5	...	....	90.9	9.1
12	10^{-12}	10^{-2}	....	2.1	97.9	...	....	50.0	50.0
13	10^{-13}	10^{-1}	....	0.2	99.8	...	....	9.1	90.9

* McKINNEY, *Ind. Eng. Chem., Anal. Ed.*, **3**, 192, (1931). Recalculated, using dissociation constants from Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York (1938).

be of the order of 10^{-3} to 10^{-2} mole per liter in order that most of the CO_2 be present as CO_3^{--}. If the hydroxyl-ion concentration is below 10^{-4} (pH = 10),[1] an appreciable fraction of the CO_2 is present as H_2CO_3. Under these conditions the CO_2 would be rapidly evolved with the steam.

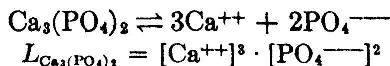
Considering now the case of phosphate treatment, it is desirable that the calcium be precipitated as $Ca_3(PO_4)_2$ rather than as $CaHPO_4$ or $CaH_4(PO_4)_2$, since $Ca_3(PO_4)_2$ is much less soluble than the other two salts and also contains a greater percentage of calcium. Reference to Table 3 again tells us that the water must be maintained fairly alkaline in order that a reasonable portion of the phosphate be present as PO_4^{---}. However, since phosphoric acid is not appreciably volatile, we need not consider its loss in the steam. Furthermore $Ca_3(PO_4)_2$ is extremely insoluble. It is found by experience that good results are obtained if the boiler water is maintained at a pH of about 10.5 ($[OH^-] = 10^{-3.5}$).

As in the case of the carbonate treatment, we consider a solution saturated with both $Ca_3(PO_4)_2$ and $CaSO_4$, under which conditions

[1] The pH value is often used to specify the hydrogen- and hydroxyl-ion concentrations. The relation of pH to these ion concentrations is given by the equation:

$$pH = \log \frac{1}{[H^+]} = \log \frac{[OH^-]}{K_w}$$

the solubility products for both salts must be satisfied.



$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{++} + 2PO_4^{---}$$

$$L_{Ca_3(PO_4)_2} = [Ca^{++}]^3 \cdot [PO_4^{---}]^2$$

Taking the cube root of this expression,

$$(L_{Ca_3(PO_4)_2})^{1/3} = [Ca^{++}] \cdot [PO_4^{---}]^{2/3}$$

and for $CaSO_4$,

$$L_{CaSO_4} = [Ca^{++}] \cdot [SO_4^{--}]$$

Since $[Ca^{++}]$ is identical in these expressions, we may write

$$\frac{(L_{Ca_3(PO_4)_2})^{1/3}}{L_{CaSO_4}} = \frac{[PO_4^{---}]^{2/3}}{[SO_4^{--}]}$$

As long as the right-hand side of this expression is maintained greater than the left-hand side, the solubility product for $CaSO_4$ cannot be attained and no scale will form.

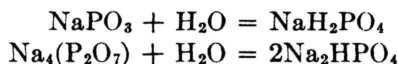
Unfortunately, neither the solubilities of $CaCO_3$ and $Ca_3(PO_4)_2$[1] nor the dissociation constants of carbonic and phosphoric acids are known at high temperatures, hence, it has been necessary to find the proper conditions for operation by trial. For phosphate treatment the amount required is so small that, if exactly maintained, practically no reserve of phosphate would be present in the boiler water, to take care of fluctuations in the quality of the feed water. It is therefore customary to maintain 25 to 50 ppm or more of phosphate (expressed as PO_4^{---}) in the boiler water.

A number of salts are available for phosphate treatment.[2] The orthophosphates, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4, sodium pyrophosphate, $Na_4P_2O_7$, and sodium metaphosphate, $NaPO_3$, are used. The quality of the feed water dictates the choice of a particular compound. For example, if the feed water tends to produce too acid a condition in the boiler, the alkaline Na_3PO_4 would be chosen. This treatment would be supplemented with NaOH if the desired alkalinity could not be maintained with Na_3PO_4 alone. If the feed water produces about the right alkalinity in the boiler, Na_2HPO_4, which is practically neutral, would be

[1] It is now believed that the solid phase produced in phosphate-treated boilers is hydroxyapatite, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$.

[2] U. S. Patents, Hall 1613656 and Hall and Jackson 1903041.

chosen. If the boiler water becomes too alkaline, the acid NaH_2PO_4 would be selected. The glassy form of $NaPO_3$, sodium hexametaphosphate, $(NaPO_3)_6$, and to a lesser extent, sodium pyrophosphate, $Na_4P_2O_7$, form soluble compounds with Ca^{++} and Mg^{++} from which the calcium and magnesium cannot be precipitated even with trisodium phosphate.[1] One of these salts, usually the metaphosphate, would therefore be chosen if the feed water contains sufficient hardness to form deposits in the boiler feed lines when the orthophosphates are used. Both the metaphosphate and pyrophosphate are rapidly hydrolyzed to orthophosphate at boiler-water temperatures.



$$NaPO_3 + H_2O = NaH_2PO_4$$
$$Na_4(P_2O_7) + H_2O = 2Na_2HPO_4$$

Their behavior within the boiler is therefore identical with the orthophosphates mentioned above. $NaPO_3$ solutions are practically neutral, whereas NaH_2PO_4 solutions are acid. The former would therefore be preferred if the use of NaH_2PO_4 causes feed-line corrosion.

Phosphate treatment for the prevention of silicate scales is the same in principle as the treatment for calcium sulfate scales. However the silicates are so much less soluble than calcium sulfate, that it has been found impossible to prevent silicate scales by internal treatment with phosphates if much silica or silicates are allowed to enter the boiler. If the water supply to the boiler contains appreciable amounts of silica, it should be removed by treatment external to the boiler, *e.g.*, by the combined magnesium sulfate-sodium aluminate treatment mentioned under the cold lime-soda process (page 12). By this means the silica can usually be reduced to a sufficiently low level so that subsequent internal treatment with phosphates will prevent the formation of calcium or magnesium silicate scales. Fortunately most water supplies contain little silica that cannot be removed by coagulation and filtration.

The use of internal treatment combined with suitable blowdown to remove sludge has contributed largely to the operation of the modern high-pressure steam boiler. Boilers can now be operated almost indefinitely without the formation of hard scale. However, it is a wise precaution to inspect them at not longer than six-month intervals, at which time sludge accumulations can be washed out.

In large boiler plants, the internal treatment is controlled by frequent analyses of the boiler water. In small plants, on ships,

[1] GILMORE, *Ind. Eng. Chem.*, **29**, 584 (1937).

or on steam locomotives, such close control is not generally provided. In these cases it is customary to prescribe a fixed treatment for the boilers, which on the average will prevent scale formation. Due to fluctuations in feed-water quality, there will be times when this treatment is insufficient and scale will form. Organic materials, such as tannin and starch, are often included in the treatment under these conditions, since it is claimed that these materials make the scale softer and easier to remove.

Cracking of Boilers

Two types of cracking have been observed in boilers. The first of these occurs at points that are obviously likely to be stressed, such as the rolled ends of tubes and the sharp angles in plates or forged parts. Because of the similarity of this type of cracking to fatigue cracking of machine parts and since the cracking is accelerated by the corrosive action of the boiler water, it has been called "corrosion fatigue." The obvious method for preventing this type of failure is to eliminate the stress concentration that causes it, by properly filleting the angles of forged parts, by eliminating sharply bent plates, and by being careful not to overroll tubes while the boiler is being assembled. Failure due to this cause has been practically eliminated in modern boilers by proper design and construction, but may be found in boilers built before about 1920. Under the microscope, corrosion fatigue cracks are found to be rather broad and transgranular and filled with corrosion products.

The second type of cracking was first observed in the riveted seams of caustic evaporators. The cracks are intercrystalline and are very fine and irregular, running from rivet hole to rivet hole and often passing one another without joining. There is little or no evidence of corrosion. Since no "necking down" can be seen, these cracks have the appearance of a brittle fracture. For these reasons this type of failure was called "caustic embrittlement." The choice of the name was unfortunate since it was later shown that the metal was not brittle nor was it possible to cause cracking by pure caustic soda, NaOH, solutions. Although intercrystalline cracking can be produced in several ways, the set of conditions necessary to produce this type of cracking in boiler operation is as follows:[1]

1. The metal must be highly stressed. The stresses may be internal residual stresses due to previous cold work or may be externally applied due to inaccurate fit of riveted parts, high riveting

[1] Schroeder, Berk, and O'Brien, *Ry. Age*, **190**, 25 (1940).

pressures, or temperature differences between the inside and outside of the riveted seam.

2. The stressed metal must come in contact with a solution capable of causing the "embrittlement." Water containing sodium hydroxide and a small amount of silica or sodium silicate may be embrittling if no protective agent is present.

3. The boiler water must concentrate at the stressed areas. It has never been possible to produce intercrystalline cracking with a dilute alkaline solution such as is ordinarily present in a boiler. The necessary concentration can occur only in restricted spaces such as are present in riveted seams. In addition, it is necessary that a slow leak be present, in order that water entering the seam may evaporate, leaving a concentrated solution behind. If the leak is too fast, the water will rush out so rapidly that concentration may not occur in contact with the stressed metal.

The first and third of these conditions can be eliminated by the use of welded boiler drums, in which case it is unnecessary to consider the character of the water. The danger of embrittlement can be minimized in riveted drums by careful design and construction to keep the stresses in seams at as low a level as possible.

From laboratory experiments, it has been found that water must contain 5 per cent or more of sodium hydroxide and a small amount of silicate to cause intercrystalline cracking. Under these conditions no corrosion takes place over the majority of the metal surface. The silica is apparently necessary for the formation of the protective film on the metal that prevents general corrosion. Corrosion occurs only at highly stressed areas and principally at the grain boundaries of the metal.

A large amount of work has been done to find inhibitors for caustic embrittlement. It was thought for many years that a high sulfate concentration would prevent cracking, but both laboratory tests and practical experience indicate that it is ineffective. Organic materials such as quebracho and the lignin contained in waste sulfite liquor from paper manufacture have been found to be very effective inhibitors up to pressures of 550 psi, and it is quite likely that many other good inhibitors will be found in the future. It has been found also that Class II Izett steel, a German steel that has been thoroughly deoxidized with aluminum, does not suffer embrittlement.

Embrittlement detectors are now available that simulate the conditions of stress and slight leakage necessary to produce crack-

ing. These may be installed on the boiler to determine whether or not the water needs treatment and to determine the effectiveness of treatment.

Wet Steam, Foaming, and Priming

Steam containing liquid water is called wet steam. A boiler producing wet steam is said to prime or foam. Steam for power production is usually superheated in order to secure greater efficiencies in the turbine or engine in which the steam is used. Wet steam causes corrosion in the inlet ends of the superheaters and, if the moisture content is high, may reduce the superheat and therefore the efficiency of the turbine or engine. Since the water in steam is boiler water, salts and sludges contained in the boiler water are carried into the superheater, where they may deposit as the water evaporates, seriously restricting the flow of steam. The insulating effect of these deposits may cause burnouts of the superheater tubes. The salts that deposit in the superheater are, for the most part, soluble in water and can be removed by flooding the superheater with water. A portion of the dried salts does not deposit in the superheater but is carried along with the steam and may then deposit on the high-pressure turbine blades or in engine valves and parts. This is especially serious in the case of turbines since a relatively small amount of deposit can decrease the efficiency of the machine appreciably. To eliminate the bad effects of moisture, mechanical steam purifiers are often installed, either in the steam drums of the boiler or between the boiler and the superheater. All these devices force the steam to take a sharply curved or tortuous path. The moisture is thrown out of the steam by centrifugal action and is either discarded or drained back to the boiler drums.

Priming may be caused by (1) the presence of foam on the surface of the water that substantially fills the steam space, (2) steam velocities sufficiently high to carry droplets of water into the steam pipe, and (3) sudden ebullition, which causes a large mass of water to be interspersed with fine bubbles.

In order to produce a foam[1] or froth on the surface of the liquid, it is only necessary that there be a distinct surface film, such as is produced by a substance in solution that concentrates either more or less in the surface layer than in the mass of the liquid and changes

[1] Weiser, "Colloid Chemistry," pp. 313–321, John Wiley & Sons, Inc., New York (1939).

the surface tension. It is immaterial whether the surface tension is increased or decreased.

The mere production of a foam in a boiler may not be objectionable, because the bubbles may break almost at the moment of forming. In order that the foam may persist for a sufficient time to fill the steam space, the film must be viscous in itself, as when soap or saponin is present, or it may be stabilized by finely divided solids provided they will enter the film. The walls of the bubbles then consist of numerous solid particles held together by films of liquid. Castor oil, which is used as an antifoam in low-pressure boilers, is probably effective because it prevents suspended matter from entering the film. Most organic substances that produce foam, such as fatty acids, the higher alcohols, and soaps, reduce the surface tension of the film, and show an optimum concentration at which the foam is most persistent. Inorganic salts and bases, which increase the surface tension, give foam stability curves which flatten out at higher concentrations. It has been shown that substances that decrease the viscosity of the film will prevent foam and also that the foaming of salt solutions (salts increase the surface tension) can be prevented by the addition of the correct concentration of substances that decrease the surface tension, such as soap. The lack of experimental data at the temperature and pressures of boiler operation and the difficulty of controlling the concentration of antifoam materials have prevented their use in boilers. "Blowing down" is the practical method for keeping the concentration of both dissolved and suspended matter below the critical foaming point in steam boilers.

Droplets of water are projected into the steam space by the breaking of bubbles, and by splashing caused by the rapid circulation of water and steam. These droplets may range in size down to the finest mist. It is therefore probable that steam velocities within a boiler operating at or near full capacity are always sufficiently high to carry fine droplets of water out of the boiler and that no boiler will produce absolutely dry steam. However, as steam velocities are decreased, the large droplets cannot be supported by the stream of steam and therefore drop back into the liquid. An effective method for reducing steam velocities is to operate with as low a water level as is possible with safety. This at the same time increases the distance a droplet must travel in order to enter the steam pipe, therefore increasing its chances of settling out of the steam. In many cases, lowering of the water

level has reduced moisture in the steam to a negligible quantity. When this does not improve the steam quality, the moisture in the steam may be due to an insufficient number or improper arrangement of steam circulating tubes.

The third cause of priming, sudden ebullition with the formation of many bubbles throughout a large mass of water, results in a sudden rise in the effective water level within the boiler. The water may reach the steam outlet and pass out with the steam. This sudden ebullition is brought about by a sudden drop in pressure in the steam line due to rapid increase in steam demand.

Summarizing, priming may be minimized by maintaining low water levels and avoiding rapid changes in the steaming rate. With a given amount of moisture in the steam, the bad effects due to the deposition of solids carried in the entrained moisture may be minimized by maintaining as low a concentration of boiler water as is consistent with scale and corrosion prevention. The maintenance of sufficiently low concentrations also prevents foaming.

Treatment for the Prevention of Corrosion

Efforts to prevent corrosion in boilers have been along two lines: the removal of oxygen from the feed water and the use of inhibitors. The removal of oxygen by means of deaerating equipment has already been mentioned. In a great many plants no additional treatment is necessary. Chemical treatment is used to remove the residual oxygen when deaeration is incomplete. Sodium sulfite is very effective if added to the feed-water system sufficiently far from the boilers so that the oxygen is consumed before the water enters the boilers. The reaction with the sulfite ion is



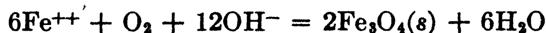
$$2SO_3^{--} + O_2 = 2SO_4^{--}$$

Ferrous sulfate and ferrous hydroxide react more rapidly with oxygen than does sodium sulfite and have been successfully used when sufficient reaction time for the sulfite cannot be attained. The reaction with the ferrous ion may be written:



$$4Fe^{++} + O_2 + 2H_2O + 8OH^- = 4Fe(OH)_3(s)$$

or if the oxygen is very low



$$6Fe^{++} + O_2 + 12OH^- = 2Fe_3O_4(s) + 6H_2O$$

Since the products of these reactions are solids, ferrous compounds are used only when the amount of oxygen to be removed is very small (0.1 ppm or less). "Deactivators," containers filled with

expanded metal or steel turnings, have been occasionally used for small low-pressure plants and hot-water heating systems. In view of the successful use of ferrous compounds in high-pressure plants, it is surprising that deactivators have not been tried in them, since, to remove a given amount of oxygen, the corrosion of iron produces only one-third as much ferric hydroxide or one-fourth as much Fe_3O_4 as the oxidation of ferrous compounds. The equation for the corrosion reaction is



$$4Fe + 3O_2 + 6H_2O = 4Fe(OH)_3(s)$$

When we consider the other method of preventing corrosion in boilers, the use of inhibitors, we find that the conditions maintained to prevent the formation of scale also provide the inhibitors necessary to prevent corrosion in the majority of cases, especially when combined with adequate equipment for the removal of oxygen. The mechanism by which inhibitors decrease the rate of corrosion is discussed in Chap. IX, page 427. In boilers both the high pH value and the presence of phosphates favor the formation of protective films of iron compounds on the surface of the metal. If the protective film covers the entire surface, no noticeable corrosion will occur. However, if the protective film is not continuous, *e.g.*, because of impurities segregated in the metal, or is periodically broken by rapid changes in temperature or by mechanical stresses, corrosion will proceed at the unprotected spot more rapidly than if no inhibitor is used. This results in "pitting" and rapid perforation of the metal. "Caustic embrittlement" is thought by some authorities to be merely an exaggerated form of pitting. No absolutely certain method for preventing corrosion in boilers has yet been devised.

Miscellaneous Treatments

Sodium metaphosphate glass at concentrations of 1 or 2 ppm has been found to be a very effective inhibitor of corrosion and also prevents the precipitation of calcium carbonate in cold-water mains or when moderately heated for short periods of time. It is widely used in recirculating cooling systems. If heated for a sufficient length of time, the metaphosphate is converted to orthophosphate and the inhibiting action therefore disappears. The use of these very low concentrations of sodium metaphosphate is called "threshold treatment."[1]

[1] *Ind. Eng. Chem.*, **29**, 584 (1937); **31**, 51 and 58 (1939); **32**, 1572 (1940).

Chromates are often used to prevent corrosion in recirculating, closed cooling systems containing either water or brine. Concentrations of 100 to 200 ppm are effective. The addition of sodium hydroxide, sodium carbonate, or trisodium phosphate also effectively reduces corrosion.

The prevention of the development of slimy deposits in condensers and coolers due to the growth of algae and other organisms in the cooling water is sometimes a serious problem. These slimes decrease the rate of heat transfer to the cooling water, causing the temperature in the steam space to rise with the result that the efficiency of the turbine decreases. In some cases condensers must be cleaned as often as twice a week to maintain the efficiency at an economical level. In small systems employing spray ponds or cooling towers, the addition of a little copper sulfate effectively prevents the growth of the organisms. In systems using water from rivers, lakes, or the sea, copper sulfate is too expensive. It is also poisonous to fish. Intermittent chlorination has proved successful in these cases. The circulating water is chlorinated for three to five minutes at regular intervals of time. The algae are killed by the chlorination, grow during the period when no chlorine is added, and are again killed by the next chlorination. The time and frequency of chlorination are adjusted to keep the condenser sufficiently clean to maintain the efficiency of the machine. The choice of chlorination or hand cleaning is of course dictated by the relative costs of the two methods and by the saving to be expected from the increased efficiency obtained by chlorination.

CHAPTER II

FUELS, COMBUSTION, AND LUBRICANTS

By David S. McKinney, D.Sc., and J. C. Warner, Ph.D.

In the present machine age, industries depend largely upon power generated by the combustion of fuels. The operation of power-driven machines requires the use of lubricants, the majority of which, together with many fuels, are obtained from crude petroleum. In this chapter, the characteristics and sources of the most important solid, liquid, and gaseous fuels will be described along with the principles involved in their combustion. The production of fuels and lubricants by the refining of petroleum is also described.

FUELS

A fuel is defined as any substance used to produce heat or power by combustion. Combustion is defined as any chemical process accompanied by the evolution of light and heat, commonly the union of substances with oxygen. Fuels constitute our most important

Table 4.—Percentage of Total B.t.u. Equivalent of Various Mineral Fuels and Water Power

Year	Pennsylvania anthracite	Bituminous	Petroleum		Natural gas	Water* power
			Domestic	Imports		
1933	7.0	45.2	28.1	1.0	8.7	10.0
1934	7.6	46.1	26.7	1.0	9.3	9.3
1935	6.6	45.1	27.7	0.9	9.5	10.2
1936	6.1	47.2	27.1	0.8	9.5	9.3
1937	5.4	45.0	29.8	0.6	9.8	9.4

* Assumes constant fuel equivalent of 4 lb. of coal per kw.-hr. If the central station rate for the year concerned is used, water power would amount to a little less than 4 per cent.

source of energy for industrial use. Although the cheapest energy is obtained from certain water-power developments, the scarcity of

suitable sites for water-power production and the poor location of many relative to the other materials required by industry make the production of power from fuels more economical in a large majority of cases. The power production from various important fuels and from water power in the United States is shown in Table 4.

The most important natural or primary fuels and prepared or secondary fuels may be classified according to their physical state as follows:

TABLE 5.—CLASSIFICATION OF FUELS

Physical state	Natural or primary fuels	Prepared or secondary fuels
Solid	Wood Peat Lignite Coal	Charcoal Briquettes Coke Petroleum coke
Liquid	Crude petroleum Natural gasoline	Tar Petroleum distillates: Gasoline Kerosene Gas oils Petroleum residues: Fuel oils Alcohol Colloidal fuels
Gaseous	Natural gas	Producer gas Water gas Mixed water gas Carbureted or enriched water gas Blast-furnace gas Acetylene

The most important property of a fuel is, of course, the amount of heat that can be obtained from it. The amount of heat is expressed in the English system in terms of British thermal units and in the metric system in terms of calories. In engineering work, the mean British thermal unit and the mean calorie are nearly always used. They are defined as follows:

The *mean British thermal unit* (B.t.u.) is 1/180 of the amount of heat necessary to raise 1 lb. of water from 32 to 212°F.

The *mean calorie*[1] (cal.) is $\frac{1}{100}$ of the amount of heat necessary to raise 1 g. of water from 0 to 100°C.

1 B.t.u. = 252 cal.

The large or kilogram-calorie (kg.-cal.) = 1,000 cal.

The heating value of solid and liquid fuels is usually reported in heat units per unit of weight, *i.e.*, in B.t.u. per pound or calories per gram.

1 cal. per g. = 1.8 B.t.u. per lb.

The heating value of gaseous fuels is generally reported in B.t.u. per cubic foot at 60°F. and 30 in. Hg.

Solid Fuels

The practical solid fuels include wood, peat, and the different varieties of coal. All these materials are of common origin, wood or the woody fibers of plants. Peat is produced by the decomposition of vegetable matter while protected from oxidation in swamps and bogs. In the carboniferous age, 150 to 250 million years ago, tremendous deposits of peat were formed, which were covered with sedimentary rocks and, under the enormous pressures and somewhat elevated temperatures incident to the folding of the earth's crust in later years, gradually lost water and volatile matter, first forming lignite and finally the various ranks of coal. This process has proceeded furthest in the anthracite coals. Many peat bogs exist today, but the rate of formation is much less than it was during the carboniferous period.

The peat bogs of the United States cover an area of about 31,000 sq. miles, and about 150,000 sq. miles of land are underlaid with lignite. These materials and wood are used as fuels in the United

[1] In scientific literature, quantities of heat are usually expressed in terms of the "defined" calorie (*a*).

1 defined calorie = 4.1833 international joules
1 defined calorie = 4.1850 absolute joules (assuming
1 international joule = 1.0004 absolute joules)
1 mean calorie (*b*) = 4.186 absolute joules
1 mean B.t.u. (*b*) = 1054.8 absolute joules

(*a*) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," p. 9, Reinhold Publishing Corporation, New York, (1936).

(*b*) "International Critical Tables," Vol. 1, p. 24, McGraw-Hill Book Company, Inc., New York (1926).

States only to a very limited extent, because of the abundance ot more desirable fuels.

The best-established classification of coals is by rank, based upon the proximate analysis. The higher rank coals are classified according to fixed carbon on the dry basis and the lower ranks according to B.t.u. on the moist basis as shown in Table 6.

TABLE 6.—CLASSIFICATION OF COALS BY RANK*

Class	Group	Dry fixed carbon mineral matter, free basis	Requisite physical properties
I. Anthracite	1. Metaanthracite	98% or more	
	2. Anthracite	92–98%	
	3. Semianthracite	86–92%	Nonagglomerating†
II. Bituminous	1. Low volatile bituminous	78–86%	
	2. Medium volatile bituminous	69–78%	
	3. High volatile *A* bituminous	Less than 69%	
		Moist‡ B.t.u. per lb. mineral matter free basis	
		14,000 B.t.u. or more	
	4. High volatile *B* bituminous	13,000–14,000 B.t.u.	Either agglomerating§ or nonweathering
	5. High volatile *C* bituminous	11,000–13,000 B.t.u.	
III. Subbituminous	1. Subbituminous *A*	11,000–13,000 B.t.u.	Both weathering and nonagglomerating
	2. Subbituminous *B*	9,500–11,000 B.t.u.	
	3. Subbituminous *C*	8,300– 9,500 B.t.u.	
IV. Lignite	1. Lignite	Less than 8,300 B.t.u.	Consolidated
	2. Brown coal	Less than 8,300 B.t.u.	Unconsolidated

* A.S.T.M. Designation D388-38. A.S.T.M. Standards (1939), Part III, p. 1.

† If agglomerating, class as low volatile bituminous.

‡ Moist B.t.u. signifies containing the natural bed moisture, but not including visible water on the surface.

§ Three varieties exist in the high volatile *C*, bituminous group: (1) agglomerating and nonweathering; (2) agglomerating and weathering; (3) nonagglomerating and nonweathering.

For classification of coal according to rank, the fixed carbon and B.t.u. are calculated from the moist basis to the mineral matter free basis by the Parr formulas:

Dry, mineral matter free, fixed carbon %

$$= \frac{F.C. - 0.15S}{100 - (M + 1.08A + 0.55S)} \times 100$$

Dry, mineral matter free, volatile matter %

$$= 100 - \text{dry, } Mm \text{ free } F.C.$$

Moist, mineral matter free, B.t.u.

$$= \frac{\text{B.t.u. (as determined)} - 50S}{100 - (1.08A + 0.55S)} \times 100$$

where Mm = mineral matter (per cent).
$F.C.$ = fixed carbon (per cent).
$V.M.$ = volatile matter (per cent).
M = moisture (per cent).
A = ash (per cent).
S = sulfur (per cent).

These formulas consider the fact that part of the sulfur is present in the ash as pyrites, FeS_2, and part in the coal substance as organic compounds.

The Analysis of Coal.[1]—The analysis of coal may be reported in two ways:

1. *Proximate analysis,* which includes moisture, volatile matter, ash, and fixed carbon (by difference). This method of analysis arose owing to the demand for laboratory tests from which conclusions could be drawn as to the applicability of the coal to a particular use.

2. *Ultimate analysis,* which includes ash, sulfur, carbon, hydrogen, nitrogen, and oxygen (by difference). The ultimate analysis is necessary in calculating heat balances in any process for which coal is used as a fuel.

The method of proximate analysis is, briefly, as follows. A gram of finely divided coal is heated at 100 to 105°C. for 1 hr. The loss in weight is reported as moisture. The dried sample is then burned in a muffle furnace at 700 to 750°C. until the weight is constant. The weight of the residue is reported as ash. The volatile matter is determined by heating a separate one-gram sample for exactly 7 min. in a platinum crucible with a closely fitting cover at a temperature of 950 ± 20°C. The loss in weight minus the moisture is the volatile matter. The fixed carbon is calculated by subtracting the percentage of moisture, ash, and volatile matter from 100.

The method for ultimate analysis follows the general procedure for all organic compounds. Hydrogen and carbon are determined by burning a weighed sample in a stream of pure oxygen in a combustion tube. Hydrogen burns to water and carbon to carbon

[1] A.S.T.M. Designation D271-37. A.S.T.M. Standards (1939), Part III, pp. 15–41.

dioxide. These are absorbed separately in suitable absorption tubes and the percentage of hydrogen and carbon calculated from the gain in weight of the absorption tubes. Nitrogen is determined by digesting a one-gram sample of coal in hot concentrated sulfuric acid containing a little mercury. The nitrogen is converted to ammonium salts by this treatment. The sample is then made alkaline with sodium hydroxide solution and the ammonia distilled into a measured amount of standard acid. The residual acid is determined by titration and the nitrogen calculated from the amount of standard acid neutralized by the ammonia. Sulfur is determined most conveniently in the bomb washings from the determination of the heating or calorific value. The sulfur is present in the washings as sulfate, from which it is precipitated as barium sulfate, filtered, ignited, and weighed. The sulfur is calculated from the weight of barium sulfate.

The heating value or calorific value is determined by burning a one-gram sample in a calorimeter and measuring the rise of temperature thus produced in the calorimeter water. The oxygen bomb calorimeter is now almost universally used. It is standardized by burning a sample of known calorific value such as naphthalene obtained from the Bureau of Standards.

Quite often the engineer is asked to estimate the thermal efficiency of a process when the calorific value of the fuel used has not been determined. Under these circumstances, formulas for calculating the calorific value from the analysis of the fuel are very valuable. When the ultimate analysis is available, the calorific value may be calculated by Dulong's formula:

$$\text{Calorific value, B.t.u. per pound} = 14{,}544\ \text{C} + 62{,}028\left(\text{H} - \frac{\text{O}}{8}\right) + 4{,}050\ \text{S}$$

where C, H, O, and S represent the fraction (per cent/100) of carbon, hydrogen, oxygen, and sulfur, respectively, in the coal. For coals low in volatile matter and oxygen, such as anthracite and low-volatile bituminous, the results are usually too high by 0.3 to 1.5 per cent. In the case of high-volatile bituminous, the calculated result may be low or high but is usually within 1.5 per cent. In subbituminous and lignitic coals, the calculated value becomes progressively too low as the oxygen content of the coal increases, the error often reaching 4 or 5 per cent.

No generally applicable formulas have been devised for calculating the calorific value from the proximate analysis, but studies made at the Bureau of Mines[1] show that the moisture- and ash-free, or moisture- and mineral-matter-free, B.t.u. of coal from a given mine and coal bed are practically constant. These quantities may be obtained from the many analyses of mine samples available in publications of the Bureau of Mines and of the various state geological surveys, and used to calculate the calorific value if the moisture, ash, and sulfur are determined on a given lot of coal. The necessary formulas are:

$$\text{B.t.u. per pound} = \frac{(\text{moisture- and ash-free B.t.u.}) \times (100 - \%\ \text{moisture} - \%\ \text{ash})}{100}$$

The B.t.u. may be calculated within 1 per cent by this formula if the sulfur does not exceed 2 per cent. If the sulfur exceeds this value, a modification of the Parr formula (page 36) may be used:

$$\text{B.t.u. per pound} = \begin{pmatrix}\text{moist.- and } Mm\\ \text{free B.t.u.}\end{pmatrix} \times \left(\frac{(100 - \%\ \text{moist.} - 1.08\,\text{ash}\ \% - 0.55\text{S}\ \%)}{100}\right) + 50\text{S}\ \%$$

Composition and Heating Values of Coals and Lignite.—Comparisons of some typical coals, made on the basis of the proximate analysis, together with heat values, are shown in Table 7.

Properties of Coal Ash.—In addition to the analysis of the coal as a whole, it is often important to know the composition of the ash, its fusibility, and how it is distributed throughout the coal. To indicate the distribution of ash throughout the coal, it is convenient to distinguish between

1. Free ash or extraneous ash, consisting of slate, clay, pyrites, etc., present in definite layers in the coal or from the roof and floor of the mine. This portion of the ash can largely be removed by washing.

2. Fixed ash or inherent ash, consisting of inorganic matter that is intimately mixed with coal or more or less evenly distributed throughout the coal substance. This ash cannot be separated by washing.

The composition of the ash, determined by the usual methods of inorganic analysis, is of great importance to the metallurgist, since

[1] Fieldner, *J. Ind. Eng. Chem.*, **5**, 270 (1913).

TABLE 7.—ANALYSIS OF REPRESENTATIVE COALS OF THE UNITED STATES*

Rank	Where mined	Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	Heat value, B.t.u. per lb.
Lignite	North Dakota	40.5	26.3	27.0	6.2	0.8	6,210
Lignite	Texas	33.5	39.5	16.2	10.8	0.6	7,140
Subbituminous	Montana	11.7	36.1	40.2	12.0	1.1	9,790
Subbituminous	Wyoming	16.5	32.9	45.8	4.8	0.6	10,750
Bituminous	Washington	6.8	40.0	47.9	5.3	1.4	12,330
Bituminous	Pennsylvania	2.7	30.4	57.8	9.1	1.3	13,610
Bituminous	Tennessee	3.4	28.2	60.1	8.3	0.8	13,430
Low-volatile bituminous	Virginia	2.7	20.0	73.9	6.0	0.5	14,495
Low-volatile bituminous	Arkansas	1.4	14.8	76.9	6.9	1.5	14,330
Semianthracite	Pennsylvania	3.3	12.5	77.9	6.3	1.0	14,340
Semianthracite	Arkansas	2.1	9.8	78.8	9.3	1.7	13,700
Anthracite	Colorado	3.0	2.9	86.6	7.5	0.7	13,500
Anthracite	Pennsylvania	2.2	5.7	86.2	5.9	0.6	13,830

* From BACON and HAMOR, "American Fuels," pp. 37–43, McGraw-Hill Book Company, Inc., New York (1922), and "Analyses of Samples of Delivered Coal," *U.S. Bur. Mines Bull.* 230 (1922).

it affects the composition of the slag and metal formed in the various metallurgical operations. The range of composition of coal ash is as follows:

	Per cent		Per cent
SiO_2	40–60	CaO	1.0–15
Al_2O_3	20–35	$Na_2O + K_2O$	1.0–4.0
Fe_2O_3	2–25	SO_3	0.2–15
MgO	0.5–4.0		

The relation of composition of ash to softening temperature or fusibility of ash is shown in Fig. 2. The fusibility of ash is important in steam generation. If the ash fuses at too low a temperature, excessive clinkering may occur on grates and melted fly ash may be deposited on the boiler tubes, interfering with heat transfer. The correlation of softening temperature with clinkering properties is not exact, since the softening temperature is determined on small cones of finely ground and intimately mixed ash whereas the clinkering may be due to segregated low-melting constituents of the coal ash.

The softening point of the ash from coals of the United States ranges from 1900 to 3100°F. This range may be conveniently divided[1] into (1) refractory ash, softening above 2600°F., (2) ash

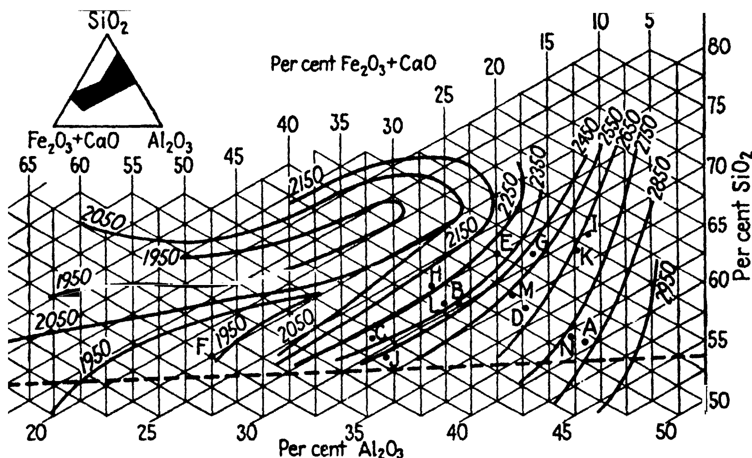


Fig. 2.—Relation of coal ash composition to softening temperature. (*Estep, Seltz, Bunker, and Strickler, Carnegie Inst. Tech., Coop. Bull.* 62, *Mining Met. Invest.*, 1934.)

of medium fusibility, softening between 2200 and 2600°F., and (3) easily fusible ash, softening below 2200°F. The A.S.T.M. specifications for gas and coking coals[2] recommend that the softening point of the ash be not below 2200°F. if the coke is to be used for domestic and industrial purposes and, if used for water-gas production, should preferably be higher than 2300°F.

Powdered Coal.—A considerable amount of pulverized coal is burned both in metallurgical furnaces and in the generation of steam. The coal is dried, either before or within the pulverizers, and is ground so that at least 65 per cent will pass a 200-mesh sieve and not more than 10 per cent remain on a 100-mesh sieve. Powdered coal can easily be transported by a stream of air or, for short distances, by screw conveyors. Since both the air and coal supplies can be accurately adjusted, almost complete combustion of the fuel may be obtained. Although the ash from coal burned on various types of grates always contains considerable amounts of combustible

[1] Selvig and Fieldner, "Fusibility of Ash from Coals of the United States," *U.S. Bur. Mines Bull.* 209 (1922).

[2] A.S.T.M. Designation D166-24. A.S.T.M. Standards (1939), Part III, p. 9.

material as compared to the ash from powdered coal, it should be remembered that this improvement was obtained at a higher cost (that of pulverizing the coal). The principal advantage in the use of powdered coal is the speed with which the rate of burning can be changed.

A disadvantage in the use of powdered coal is the fineness of the ash particles produced, much of which will pass a 325-mesh sieve. A large proportion (roughly 75 per cent) of the ash is therefore carried out the stack by the exhaust gases. The amount of fly ash is less if powdered coal is burned in a "slag tap" furnace in which the flame is directed toward and sweeps over a bed of molten slag where the particles of ash are caught. The molten ash is removed from time to time by tapping the slag pit.

The softening temperature of the ash is very important in the combustion of powdered coal in boilers, as the flame is hot enough to melt the ash particles. If these particles arrive at the boiler tubes before they have been cooled below the softening temperature, the molten particles will adhere to the tubes and decrease the rate of heat transfer.

The Secondary Solid Fuels.—The secondary solid fuels include charcoal, briquettes, and coke. Charcoal, the residue from the destructive distillation of wood, is not an important commercial fuel. The term "briquette" includes compressed fuel made from coal, lignite, peat, or coke, either with or without a binder. In Europe, where coal is scarce and much of it is low grade, the briquetting industry is quite extensive but, in the United States, the cost of good quality coal is so low that briquetted fuel is uneconomical. Briquetting will become more important as our best seams of coal are depleted, since it provides a method of utilizing the small-sized waste coal produced in mining. In the usual briquetting process, the fine coal is mixed with 5 to 8 per cent of binder and formed into briquettes at pressures of 1,800 to 3,000 psi in a roll press. Commonly used binders are asphalt pitch and pitch from coal tar or water-gas tar. Other binders are gilsonite, molasses, starch or dextrin pastes, and sulfite liquor from the paper industry. After pressing, the briquettes may be baked to remove a portion of the volatile matter and, if pitch has been used as a binder, the objectionable cresols that they contain.

Coke is usually defined as the residue remaining after coal has been heated strongly out of contact with the air, a process now generally termed carbonization. The carbonized residue remaining

in the stills after distillation of petroleum residues to dryness is known as petroleum coke and comprises about 0.5 per cent of the total weight of petroleum refined. Because of the small amount produced, petroleum coke is not an important industrial fuel. If the carbonization of coal is carried out at 500 to 700°C., the product is known as low-temperature coke. The coke thus produced contains 5 to 15 per cent of volatile matter and is not sufficiently strong to be used as a metallurgical fuel. Since it is easily ignited, it is a valuable smokeless fuel. The gas produced by the low-temperature coking process is richer than that produced in the high-temperature coking process (675 to 1,000 B.t.u. per cu. ft. depending on the coal and the process used) and is therefore a more valuable gaseous fuel. The low-temperature coking process is carried out both with coking and noncoking coals. When the coke is too friable for use as a fuel directly, it may be briquetted or pulverized. A comparison of the products obtained by the low- and high-temperature carbonization processes is given in Table 8.

TABLE 8.—PRODUCTS FROM HIGH- AND LOW-TEMPERATURE CARBONIZATION

Product	High-temperature carbonization (by-product ovens)	Low-temperature carbonization
Coke:		
Pounds per 100 lb. coal	65–75	75–80
Volatile matter in coke	1–3 per cent	5–15 per cent
Gas:		
Cubic feet per ton	10,000–13,000	4,000–9,000
B.t.u. per cubic foot	530–600	675–1,000
Light oil and tar, gallons per ton	10–17	18–49
Ammonium sulfate, pounds per ton	24–26	12–15

High-temperature carbonization is carried out at final temperatures between 900 and 1100°C., and has as its primary purpose, the production of metallurgical coke. For metallurgical purposes the coke must be strong enough to bear the burden to which it is subjected and to resist shattering during handling. Coals that will produce coke of useful grade are called coking coals. A good coking coal, such as that from the Connellsville district in Pennsylvania, will produce a bright gray, strongly coherent, porous coke. High-volatile coals yield light, friable cokes. When such coals are mixed with poor or noncoking low-volatile coals, the resulting mixture will

yield a denser, stronger coke. Where mixing is practiced, the mixture used depends on the coals being coked; usually high- and low-volatile coals are mixed in such proportions as to give a mixture having about 30 per cent of volatile matter. The other characteristics desired in metallurgical coke are discussed on page 261.

The coking results from the decomposition of the tarry constituents of the coal, and the separation of carbon or substances rich in carbon. In a general way, the changes that take place during coking are shown by the following percentage analysis of a coke and the coal (Pennsylvania bituminous) from which it was made:

	Water	Volatile combustible	Fixed carbon	Sulfur	Ash
Coal	4.50	25.40	64.25	0.87	5.85
Coke	....	0.73	90.49	0.78	8.78

Because of the loss of volatile matter, the percentage of ash in the coke is higher than in the coal; and, for the same reason, more sulfur has been removed by coking than might seem apparent from the percentage shown. It should be noted that the sulfur-to-carbon ratio has been considerably reduced.

An important advantage of coke as a fuel is its porous structure; its apparent specific gravity is about 0.9, while its true specific gravity is about 1.90; consequently, approximately 50 per cent of its volume is air space. This cellular structure enables the coke to burn more readily. Coke averages about 13,000 B.t.u. per lb.

Coking Processes.—There are two processes for making coke, named according to the character of the oven in which the distillation is carried out.

One type, the *beehive oven*, illustrated in Fig. 3, is a dome-shaped oven of brick, 12 to 13 ft. in diameter and 7 to 8 ft. high inside. It has an opening in the top through which the coal is charged and a door in one side through which the coke is removed and through which a small amount of air is admitted. The ovens are constructed in long rows, some of which are a quarter of a mile in length. Alternate ovens are charged with sufficient coal to produce, when leveled off, a layer about 2 ft. deep. Meanwhile the intermediate ovens are burning at full heat and the heat from the hot ovens passing through the party wall ignites the charge in the adjacent oven.

Only enough air is admitted through the door in the side to produce an amount of burning sufficient to keep the temperature at the desired point. The heat furnished by this partial combustion

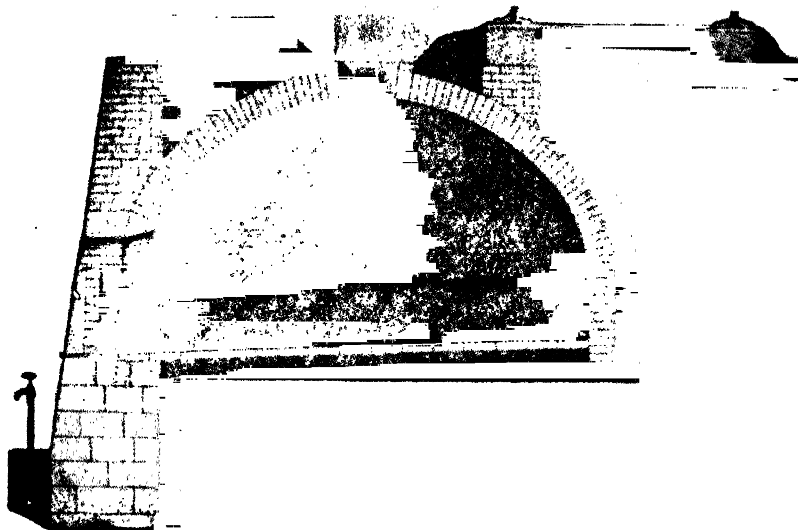


FIG. 3.—Standard American beehive coke oven.

causes the coal to melt or fuse and give up its volatile constituents. The time that the charge is allowed to remain in the oven is usually 48 or 72 hr. The longer the time, the harder the coke, and the less residual volatile matter it will contain. The 72-hr. coke is usually that which is allowed to remain in the oven over Sunday. Because of its hardness, this coke is most desired by the foundry man. In the beehive oven, the yield of coke is about 60 per cent of the coal charged, and averages about 5 to 5½ tons of coke per oven.

The other type of oven is the *by-product oven,* of which one well-known type is illustrated in Fig. 4. The narrow rectangular oven chambers are about 37 to 42 ft. long, 10 to 14 ft. high, and 14 to 18 in. wide. They are tightly closed so that no air is admitted; the heat for coking is furnished by burning gas in flues contained in the side walls of the ovens.

The ovens may be heated either by a low B.t.u. gas, such as producer gas or blast-furnace gas, or else by part of the coal gas produced in the coke oven itself. Where producer gas or blast-furnace gas is used for underfiring, the total coke-oven-gas produc-

tion of about 11,000 cu. ft. per ton of coal is available for sale for city use or industrial purposes. If, on the other hand, part of the coke-oven gas is used for underfiring, the surplus gas amounts to about 6,000 to 6,500 cu. ft. of gas per ton of coal. The coking time ranges generally from 12 to 20 hr., and the coke yield is about 70 per cent of the coal charged, or about 7 to 13 tons per oven.

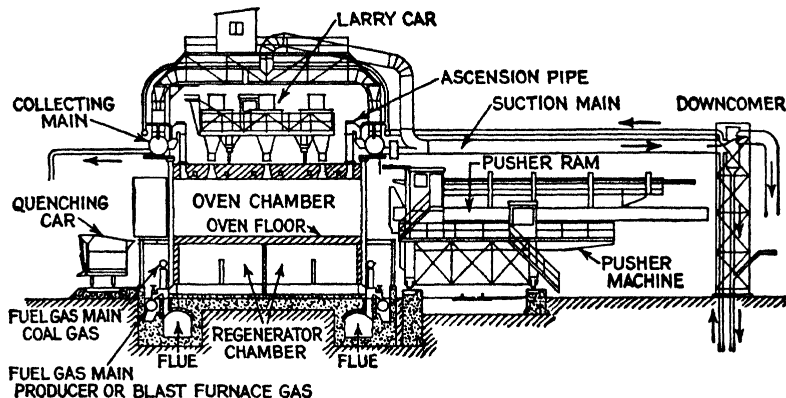


FIG. 4.—Cross section through a by-product coke oven. (*Courtesy of The Koppers Company. Reprinted by permission from Read, "Industrial Chemistry," John Wiley & Sons, Inc.*)

In the by-product coke oven the valuable by-products are saved; in the beehive oven they are allowed to escape into the atmosphere to become a great nuisance as well as being a great waste. The by-products are well worth saving and have many important uses. Their recovery helps to make by-product coke-oven operation economical. The products obtained from high-temperature, by-product ovens are listed in Table 8.

In the purification of the by-product-oven gas by means of a liquid-contact process, the Koppers Co. obtains practically pure sulfur in a form much finer than the commercial precipitated sulfur. This finely divided sulfur has been found to possess superior qualities as a fungicide.[1] Among the other interesting and valuable by-products recovered by the liquid-purification processes are the thiocyanates of ammonium, sodium, and calcium.

Production by Processes.—Fortunately, the coking of coal by the beehive-oven process is now less common than formerly, as the following figures show. Because of the ease with which beehive-coke production can be expanded, the process will probably continue to be used during periods of rapid industrial expansion.

[1] RAMSBURG, *Mining Congr. J.*, February, 1930, p. 69.

Percentage of Total Production of Coke

Year	By-product-oven coke	Beehive-oven coke
1909	15.91	84.09
1914	32.47	67.53
1919	56.90	43.10
1923	66.00	34.00
1927	91.5	8.5
1934	96.8	3.2
1937	94.0	6.0

Comparison of Cokes.—The beehive-oven coke, which has a clean, silvery gray appearance, usually occurs in long, slim pieces, commonly designated as "fingery" coke. The by-product-oven coke, of a gray-black cast, occurs in short, thick pieces. The difference in surface appearance is affected by the manner of quenching. In the beehive oven, the coke is quenched within the oven, and as little water as possible is used. In the case of the by-product oven, the red-hot coke is pushed out into a coke car, which carries it to the quenching station where it is showered for a definite short period of time by a spray of water. The coke is then exposed on an inclined wharf, to allow the remaining internal heat to drive off surface moisture. No matter how quickly the coke may be quenched after being forced from the oven, contact between the air and the highly heated coke will have occurred. This causes a certain amount of surface oxidation, which destroys the luster of the coke.

The wet quenching of coke offers a means of disposal, from by-product plants, of the waste liquors that cannot be discharged into streams. When these liquors can be disposed of in other ways, "dry quenching" offers advantages. In this method, the hot coke is placed in a chamber and cooled with inert gases (largely nitrogen) from the boilers. The heated gases are then circulated to the boilers, where they generate steam. In addition to generating about 1,000 lb. of steam per ton of coke quenched, this method eliminates the pumps and other wet quenching equipment and reduces corrosion problems. The coke produced is cleaner and drier, and contains less dust and breeze than wet-quenched coke.

The size and shape of the lumps of by-product-oven coke are advantages. Since the lumps are generally of a uniform size, the space between them is greater; therefore, the furnace blast can pass with greater ease. The prejudice against by-product-oven coke,

which was strongly marked until a few years ago, has been overthrown by the actual demonstration that such coke, when properly made and used, is actually superior to beehive-oven coke.[1]

Coke as a Metallurgical Fuel.—The greatest amount of coke produced is used as a metallurgical fuel, chiefly for iron. For this purpose, it is far more desirable than coal because it contains less sulfur and because it is able to support the weight of the charge, which soft coal cannot do.

Coke is less desirable than charcoal, from the standpoint of chemical composition, because it contains more sulfur, phosphorus, and ash. But because of the greater cost of charcoal its use is limited; coke is far more widely used. The fact that coke is stronger than charcoal is also an important consideration, for, since it can support a greater weight, higher furnaces can be built.

From the coke practically all of the phosphorus and some of the sulfur are taken up by the iron; the ash must be cared for as slag. The sulfur content of coke is its most objectionable feature. This varies from 0.5 per cent in the best cokes to 2 per cent in inferior cokes. In the ordinary good coke the sulfur will vary from 0.5 to 1.25 per cent. Phosphorus is generally not high, usually under 0.05 per cent.

The ash of coke varies from 6 per cent in extremely good cokes to 14 or 16 per cent in those of poor quality. Usually the ash ranges from 8 to 12 per cent. The ash of a coke may be materially decreased by washing the coal prior to coking, and a low ash content is of great importance in the economical operation of metallurgical furnaces.

Liquid Fuels

As indicated in Table 5, the important liquid fuels are tar, petroleum and petroleum products, alcohols, and colloidal fuels. Of these, the fuels of less commercial availability will be considered first. The liquid fuels offer the following advantages over solid fuels:

1. The fuel may be stored at a distance from the furnaces and in tanks of irregular shape. The latter is of particular importance on shipboard, since it makes use of space that cannot be used for cargo or other purposes.

2. The fuel is handled with very little labor, and the work of cleaning fires and handling ashes is eliminated.

[1] Bacon and Hamor, "American Fuels," p. 121, McGraw-Hill Book Company, Inc., New York (1922).

3. Fuel is immediately available, and the rate of burning can be changed very rapidly.

4. Fuel oils weigh 30 per cent less and occupy 50 per cent less space than coal of equal heating value.

5. Liquid fuels are not spontaneously combustible and, if not volatile, do not deteriorate during storage.

The principal advantage of liquid fuels over gaseous fuels is the ease of storage.

Tar.—Tar from by-product coke ovens offers the advantages of a liquid fuel, except that it is difficult to keep in the liquid state. The tar must be heated and screened or filtered while hot. A large proportion of by-product tar is used, together with coke-oven gas, in heating open-hearth furnaces in the steel mills. The heating value of tar is 15,000 to 16,500 B.t.u. per lb.

Alcohol.—Ethyl alcohol is not a commercially important fuel at present, because of the high cost of its production relative to that of petroleum products. It can be burned in internal-combustion engines, either pure with special carburetors, or mixed with gasoline with slight or no modification of the carburetors used for gasoline alone. It is a possible fuel of the future, especially as a substitute for gasoline. The heating value of ethyl alcohol is 12,390 B.t.u. per lb.

Colloidal Fuel.—Colloidal fuel is an emulsion of solid fuel in oil. The solid fuel, which may be coal, peat, coke, or wood, is pulverized so that 95 per cent will pass a 100-mesh sieve and 85 per cent will pass a 200-mesh sieve. The solid fuel is then mixed with oil to which a "fixateur" has been added to prevent settling of the solid fuel particles, and is then ground in a ball or tube mill to secure intimate mixing. Lime-rosin grease or creosote may be used as a fixateur. Colloidal fuel containing approximately 30 per cent of coal has a heating value of about 17,000 B.t.u. per lb. and can be fired in ordinary oil-burning equipment.

Fuels from Petroleum.—Petroleum is by far the most important source of liquid fuels. As indicated in Table 4, about 30 per cent of the energy used in the United States is derived from it. Since the refining of petroleum will be considered later in this chapter, we shall consider here only the properties of those products used as fuels.

Fuel Oil.—Fuel oil is defined as any liquid or liquefiable petroleum product used for heat generation in a firebox or for power generation in an engine, exclusive of oils with flash points below

100°F. and oils burned in cotton or wool wick burners. Common fuel oils are:

1. Residual fuel oils, which are topped crude petroleums or viscous residuums obtained in refinery operations.

2. Distillate fuel oils, which are distilled products derived from petroleum and are usually the fractions distilled intermediate between kerosene and lubricating oils.

3. Crude petroleums and weathered crude petroleums.

4. Blended fuels, which are mixtures of the above.

The crude petroleums used as fuel oils are usually those of low commercial value, especially those containing small amounts of volatile constituents. Crude petroleums that have lost an appreciable quantity of the more volatile components due to natural causes during storage or handling are called weathered crude petroleums. Topped crude petroleum is the product remaining after removal, usually by distillation, of an appreciable quantity of the more volatile components of crude petroleum. The unrefined distillate so obtained is called "tops."

Specifications for various grades of fuel oil recommended by the American Society for Testing Materials are listed in Table 9. In order that the fuel oil be burned efficiently and rapidly, it must be atomized or vaporized in a suitable burner. The more viscous oils are preheated to aid in atomization and to assure their flowing easily to the burner. The various types of burners used are

1. The spray-type burner, in which the oil is atomized by the shearing action of a stream of air or dry steam. Air, when available, has the advantage over steam that it supplies a part of the air necessary for combustion, and also avoids the loss of the heat in the steam. In addition, low-pressure air allows more accurate adjustment of the burners.

2. The rotary-type burner, in which the oil is fed to the inner portion of a revolving hollow cone. The centrifugal force of the rapidly revolving cone causes the oil to fly off the edge of the cone in small droplets. Air is supplied to the annular space around the cone by means of a fan, which is often on the same shaft as the revolving cone. The blast of air from the fan further atomizes the oil.

3. Mechanical spray burners, in which oil at high pressure and temperature passes out of small orifices. The atomization is accomplished partly by the spraying action of the orifices and partly by the sudden vaporization ("flashing") of the more volatile portion

TABLE 9.—SPECIFICATIONS FOR FUEL OIL—A.S.T.M. D396-39T

Grade	Sulfur, %	Flash point, °F.		Pour point, °F.	Water and sediment, %	Carbon residue, % (Conradson)	Ash, %	Distillation temp., °F. 10% point	90% point		End point	Viscosity: Saybolt Universal at 100°F.		Saybolt Furol at 122°F.	
	Max.	Min.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Min.	Max.	Max.	Min.	Max.	Min.
No. 1 for burners requiring a volatile fuel.	0.5	100 or legal	165	0	Trace	0.05 on 10% residuum	....	410	...	...	560				
No. 2 for burners requiring a moderately volatile fuel.	0.5	110 or legal	190	10	0.05	0.25 on 10% residuum	....	440	600						
No. 3 for burners requiring a low viscosity fuel.	0.75	110 or legal	230	20	0.10	0.15	....	...	675	600	...	45			
No. 5 for burners requiring a medium viscosity fuel.	No limit	130 or legal	...	..	1.00	....	0.10	...	...	...	...	..	50	40	
No. 6 for burners with preheaters permitting a high viscosity fuel.	No limit	150	...	..	2.00	....	....	...	...	...	...	..	..	300	45

of the hot oil due to the decrease in pressure in passing out of the burner.

4. Vapor-type burners, in which the oil is evaporated by a stream of preheated air. These burners are limited in application to furnaces where the stack temperatures are sufficiently high to preheat the necessary air, as in forging, annealing, and tempering furnaces.

Heating Value of Fuel Oils.—The heating value of fuel oils is usually reported in terms of B.t.u. per pound, and for most fuel oils lies between 18,000 and 19,500 B.t.u. per lb. Fuel oils are practically always sold on a volume basis, the volume being measured at or corrected to 60°F. Tables for making the correction to 60°F. have been published by the Bureau of Standards (*Circular* C410) and by the A.S.T.M. (Designation D206-36). A fact not always appreciated by purchasers of fuel oils is that, although an oil of high specific gravity (low A.P.I. gravity) may have a lower heating value per pound than one of low specific gravity (high A.P.I. gravity), the reverse is true when the heating value per gallon is considered. It is also usually true that the cheapest oils per gallon have the highest B.t.u. per gallon. The heating value of crude oils may be calculated roughly from the A.P.I. gravity by the following formula:

$$\text{B.t.u. per pound} = 17{,}820 + 57.33 \times (\text{degrees A.P.I.})$$

The A.P.I. gravity is a variation of the Baumé scale, which has been approved by the American Petroleum Institute as a standard, and is now used almost exclusively in specifying petroleum products. It is related to the specific gravity by the following formula:

$$\text{Degrees A.P.I.} = \frac{141.5}{\text{specific gravity, } 60°/60°\text{F.}} - 131.5$$

It should be noted that as the specific gravity increases, the A.P.I. gravity decreases.

Two other Baumé scales are in common use for liquids other than petroleum products and are inserted here for comparison with the A.P.I. scale. For liquids heavier than water,

$$\text{Degrees Baumé (°Bé)} = 145 - \frac{145}{\text{specific gravity, } 4°/4°\text{C.}}$$

and for liquids lighter than water,

$$\text{°Bé} = \frac{140}{\text{specific gravity, } 4°/4°\text{C.}} - 130$$

Diesel Engine Fuel Oils.—Low-speed diesel engines can be designed for a large range of fuel oil quality. In some cases even blends of crude residuums with heavy gas oils are used. Oils must be avoided that form excessive amounts of carbon on ignition.

In high-speed diesel engines, oils must be selected that ignite quickly upon compression, a property opposite to that required by gasoline engines. The property of easy ignition on compression parallels the "paraffinic" quality of the oil and is characterized chemically by a high ratio of hydrogen to carbon. The attainment of good ignition properties in diesel oils of the higher boiling ranges is accompanied by an increase in the wax content of the oil. Increase in the wax content causes an increase in the pour point of the oil, but the wax content should be as high as possible, because of the improved diesel ignition quality. Most diesel engine oils fall in the class known as "gas oils," which are defined as liquid petroleum distillates whose viscosities fall between that of kerosene and lubricating oils.

Kerosene.—Kerosene is a refined petroleum distillate, whose flash point is not less than 73°F. and which is suitable for use as an illuminant in wick lamps. Although less important than formerly, considerable quantities of kerosene are used as a fuel in farm tractors and as an illuminant.

Gasoline.—Gasoline production represents 43.9 per cent of the total petroleum produced in this country, and 89 per cent of the gasoline is used in motor vehicles. Gasoline belongs to that class of petroleum products called "petroleum naphthas," which are defined as petroleum products or products of natural gas, of which not less than 10 per cent distills below 347°F. and not less than 95 per cent below 464°F. Gasoline is a refined petroleum naphtha suitable for use as a carburant in internal-combustion engines. In order to fulfill the requirements of modern gasoline engines, gasoline must have the following characteristics:

1. It must be sufficiently volatile to permit of easy starting, yet not so volatile as to cause vapor lock under the prevailing climatic conditions. These properties are attained by controlling the distillation range and the vapor pressure as indicated in Table 10.

2. It must be comparatively free from gum-forming constituents and from objectionable sulfur and other corrosive materials.

3. It must be reasonably stable in storage.

4. It must possess "antiknock" properties suited to the modern high-compression engine. The antiknock properties are indicated

by the "octane number," which will be more fully discussed later in this chapter. The heating value of gasoline lies in the range 19,000 to 20,500 B.t.u. per lb.

Specifications for three types of gasoline, covering the requirements for ordinary usage, are given in Table 10. These specifications do not cover all requirements, for certain types of trucks and busses may need gasoline of lower volatility (lower vapor pressure and higher distillation temperatures) and airplane engines require gasoline having superior antiknock properties.

TABLE 10.—SPECIFICATIONS FOR GASOLINE—A.S.T.M. D439-40T

Gasoline*	Distillation temp., max. °F.					Distillation residue—max. %	Vapor pressure max. psi at 100°F.			Octane‡ number, min.	Gum—max. mg. per 100 ml.	Corrosion
	10 % evaporated			50 % evaporated	90 % evaporated							
	W†	*F*†	*S*†				*W*	*F*	*S*			
Type *A*....	140	149	158	284	392	2	13.5	11.5	9.5	70 or 77	7	Passes
Type *B*....	140	149	158	257	356	2	13.5	11.5	9.5	70 or 77	7	Passes
Type *C*....	167	167	167	284	392	2	13.5	11.5	9.5	50	7	Passes

* Type *A* gasoline is for use under normal conditions. Type *B* is for use where a gasoline of greater over-all volatility than type *A* is desired. Type *C* gasoline is for use where a relatively nonvolatile fuel is desired.

† *W*, *F*, *S* indicate automatic seasonal variation. In general, *W* indicates winter grade, *S* summer grade, and *F* fall and spring grade, but the specification permits of variation according to the prevailing temperature in a given region.

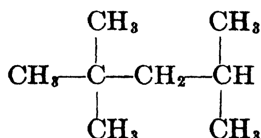
‡ 77-octane number, minimum, is premium priced gasoline. 70-octane number, minimum, is regular priced gasoline. 50-octane number, minimum, is less than regular priced gasoline.

Gasolines may be classified according to their source into natural, straight-run, cracked, and polymer gasolines. The last two classes will be discussed under petroleum refining. Natural gasoline is obtained from natural gas either by compression and refrigeration, or more commonly by absorption in gas oil and subsequent steam distillation. Natural gasoline provides about 9 per cent of our supply. It is too volatile for use alone as motor fuel and is therefore blended with refinery gasolines to improve their volatility.

The distillation of crude oil produces a certain amount of low-boiling naphtha, having the correct volatility for use as motor fuel. This is known as straight-run gasoline.

"Antiknock" Properties of Gasoline.—In internal-combustion engines, the ratio of the cylinder volume at the end of the down-stroke to the volume at the end of the upstroke of the piston is

called the "compression ratio." The higher this ratio, the more the fuel-air mixture is compressed before explosion and the higher is the efficiency of the engine. The rapid compression of the fuel-air mixture in the modern high-compression engine heats it to the point that premature ignition may occur, causing "knocking," if easily ignited fuels are used, such as straight-run gasoline. The antiknock value of a motor fuel is expressed quantitatively in terms of "octane number," which is determined by matching the knocking characteristics of the fuel being tested with those of mixtures of normal heptane and isooctane in a standard single-cylinder engine of variable compression ratio, by a carefully standardized procedure (A.S.T.M. D357-39). The percentage by volume of isooctane in the isooctane-heptane mixture that matches the knocking characteristics of the fuel being tested is called the octane number. Normal heptane, C_7H_{16}, has about the *poorest* antiknock properties of all pure compounds suitable as fuels for internal-combustion engines; isooctane,



has very good antiknock properties. From the definition of octane number, it will be seen that pure normal heptane has an octane number of zero and pure isooctane an octane number of 100.

Studies have shown that gasoline of low hydrogen-to-carbon ratio, from naphthenic and asphalt base crudes, have high octane numbers and low volatility; the reverse is true of gasoline from paraffinic crudes. Cracked gasolines have generally higher octane numbers than straight-run gasoline from the same crude, the octane number of the cracked gasoline increasing with the temperature of cracking. The properties of the various types of gasolines have been coordinated with the types of hydrocarbons that they contain. The knocking tendency of paraffin hydrocarbons increases with the length of the hydrocarbon chain. Butane has an octane number of nearly 100, and heptane, as we have seen, has an octane number of 0. Because of the high octane number of butane, a maximum quantity of it is included in the gasoline. Branched-chain hydrocarbons such as isooctane have much less tendency to knock than do straight-chain hydrocarbons. The high octane numbers of high-grade aviation gasolines are obtained by the use of highly branched

hydrocarbons similar to isooctane. Double bonds and cyclic structures improve the antiknock properties of hydrocarbons. The aromatic hydrocarbons have less tendency to knock than the naphthenes.

The cracked gasolines contain higher percentages of unsaturated and cyclic hydrocarbons than are present in straight-run gasolines, which accounts for their improved antiknock properties. Because of the presence of the unsaturated hydrocarbons, particularly the olefins and diolefins, the cracked gasolines are less stable than straight-run gasoline and tend to form objectionable gums. Recently, inhibitors have been discovered, as little as 0.001 per cent of which effectively slow down the gum formation and provide sufficient stability during storage (page 91).

If gasolines, produced in the refinery process, are not up to the desired octane rating, they may be improved by the addition of tetraethyl lead, $Pb(C_2H_5)_4$, the only antiknock of commercial significance. Ethylene bromide is added to the gasoline with the tetraethyl lead so that the lead will be converted to lead bromide when the "ethyl gasoline" is burned in the engine, and the lead bromide expelled with the exhaust gases. The greater the paraffinic quality of the gasoline, the greater its response to tetraethyl lead additions. Since tetraethyl lead is extremely toxic, great care should be exercised in handling fuels containing it.

Gaseous Fuels

The ease and flexibility of application of gaseous fuels give them advantages over solid or liquid fuels, which may be summarized as follows:

1. The combustion may be readily controlled for changes in demand, the oxidizing or reducing nature of the flame or atmosphere, the length of flame, and the temperature.

2. Greater thermal efficiency can usually be obtained when high temperatures are required, since a good portion of the heat in the stack gases may be recovered by regeneration or recuperation.

3. Smoke and ash are eliminated, and there is no labor involved in fuel or ash handling.

4. Low-grade solid fuels may be more economically utilized after gasification and, under certain circumstances, it may even be economical to gasify high-grade coal at one point and distribute the gas over a wide area. The production of coal gas renders possible the recovery of by-products such as ammonia, benzene, and toluene.

5. Gas may be used in internal-combustion engines for the direct production of power.

The sources or methods of production and composition of the various gaseous fuels will be considered first. The composition and heating value of typical gaseous fuels are summarized in Table 11.

Natural Gas.—The origin of natural gas is closely associated with that of petroleum; it is always found in or near the petroleum fields. Because of this fact, it is not available over large sections of the country, although pipe lines are being constantly extended to furnish gas to large consuming centers, where it may be used either alone or mixed with artificial gas. In the past, large volumes of natural gas were wasted when struck during drilling operations for petroleum. Nowadays, the tendency is toward the use of the gas for repressuring oil fields in which the yield is declining. About 14 per cent of the gas produced is used for making carbon black. Exhausted gas wells near locations where the gas is consumed may be conveniently used to store gas from more distant producing wells.

Natural gas, as supplied to the user, consists largely of methane and ethane, but raw gas from the wells may contain higher hydrocarbons, which are removed and sold as natural (casing-head) gasoline. In 1937, 2,370 billion cu. ft. of natural gas were produced, the chief producing states being Texas, California, Louisiana, Oklahoma, and West Virginia. Eighty-six per cent of this gas was treated for natural gasoline recovery.

Natural gas contains only small percentages of noncombustible gases and has the highest kindling temperature and highest calorific value of all the gaseous fuels.

Producer Gas.—Producer gas is an artificial gas resulting from the incomplete combustion of a solid fuel (coal or coke) in a partly closed generator of special construction known as a gas producer. There are many forms of producers, each embodying usually some special feature. One of the several types is shown in Fig. 5. In the United States all the producer gas is made by admitting a mixture of air and steam to the bottom of the gas producer. Upon reaching the combustion zone, the oxygen of the air is consumed to form carbon dioxide by the reaction: $C + O_2 = CO_2$ (exothermic). The hot gases from the combustion zone heat the fuel in the reduction zone to incandescence, where the following reactions take place:



$$C + CO_2 = 2CO \text{ (endothermic)}$$



$$C + H_2O = CO + H_2 \text{ (endothermic)}$$

These are the principal fuel-making reactions. Since they are endothermic, the gas stream cools off in passing through the reduction zone. When bituminous coal is used in the gas producer, the hot

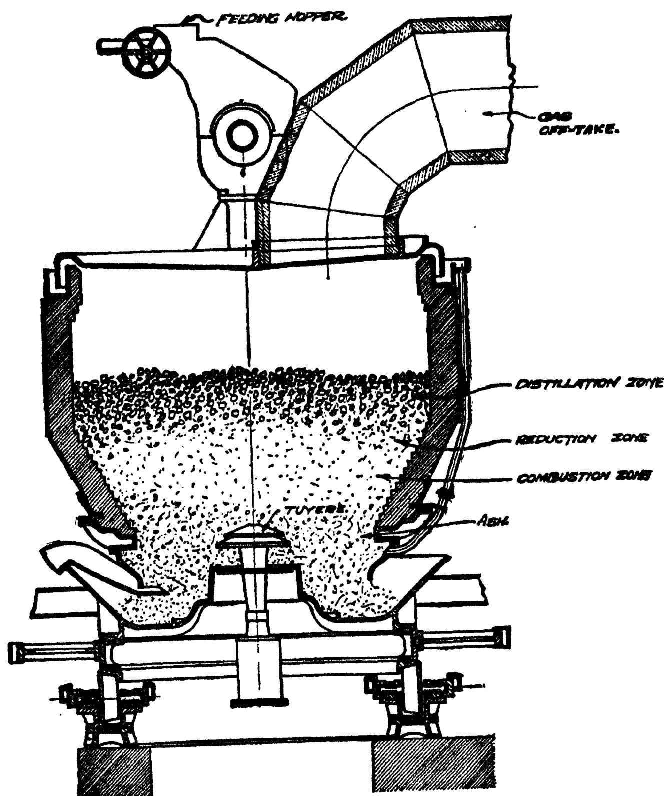


FIG. 5.—Cross section of a gas producer.

gases rising into the distillation zone remove the volatile part of the coal, which provides the methane and ethane in the resulting gas. The temperature of the gas leaving the producer should not exceed 1250°F. and should be of a golden yellow color. When coke is used as fuel, the concentrations of methane and ethane are reduced to traces. Raw gas made from bituminous coal also contains tar and other products of coal distillation. These are not included in the analyses given in Table 11, which represent clean washed gases. When low-ash, high-volatile coal is used, about 52 cu. ft. of air and 0.20 lb. of steam are required to gasify 1 lb. of coal. The amount of steam used must be great enough to keep the temperature in the pro-

ducer below the fusion temperature of the ash in order to avoid clinkering. In the manufacture of producer gas the aim is to produce a gas containing no CO_2, but this aim is never quite attained, as the analyses indicate.

The product that we have called producer gas was formerly called mixed or semiwater gas. Another artificial gas sometimes called producer gas, but more accurately described as Siemens gas or air gas, is made by blowing air alone through the gas producer. It contains only a small percentage of hydrogen from the moisture in the air used, and the moisture and hydrogen in the fuel. Since the over-all reaction, $2C + O_2 = 2CO$, is exothermic, the production of air gas results in very high temperatures in the gas producer, causing trouble due to clinkering of the ash. The resulting gas also has the very low heating value of about 110 B.t.u. per cu. ft.

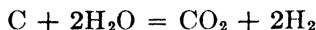
Water Gas.—The principle involved in the manufacture of water gas is essentially the same as in making producer gas, except that in the former, the air and steam are blown in at alternate intervals. Air is first forced through the coals in the producer until a high degree of heat is reached, which process itself makes a low-grade gas containing some carbon monoxide. This low-grade gas is used for heating purposes around the plant.

When the bed of coals is sufficiently hot, the air is cut off and steam is blown in. The steam reacts with the incandescent carbon to form hydrogen, and either carbon monoxide or dioxide, depending upon conditions. If the temperature of the carbon is above 1000°C., the reaction proceeds as follows:



$$C + H_2O = CO + H_2$$

but if the temperature falls below 1000°C., the following reaction occurs:



$$C + 2H_2O = CO_2 + 2H_2$$

Since both carbon monoxide and hydrogen burn with a non-luminous or blue flame, water gas is sometimes known as "blue gas." Water gas is used either alone as a fuel or as a constituent of illuminating gas. If used for illumination, the blue gas must be enriched with hydrocarbons, in which case it is said to be carbureted.

The process of making water gas is modified, then, according to the purpose for which the gas is to be used. If it is used for a fuel gas, the products of combustion resultant from the blowing in of air may serve to preheat the incoming air or steam, or may be

allowed to escape. If used for illuminating gas, the products resultant from the air blast are burned to heat a checkerwork of brick, which is used to gasify the vapors of petroleum oil used in carbureting. The blue gas is first mixed with the oil vapors and this mixture is then conducted through the hot checkerwork where the hydrocarbon vapors are decomposed and fixed in permanent gaseous form.

According to the primary equation of formation, a theoretical water gas would contain 50 per cent each of carbon monoxide and hydrogen. An actual analysis of the blue gas shows small percentages of carbon dioxide and nitrogen. Since water gas contains such a high percentage of carbon monoxide, which is odorless and extremely poisonous, much danger attends its use. Small amounts of materials having very penetrating odors are sometimes added to the gas to give warning of leaks.

Blast-furnace Gas.—This is the waste gas issuing from the top of the blast furnace. It is recovered and used either in the Siemens regenerator or stove to preheat the blast for the furnace, or in gas engines. Also it may be used beneath the boilers for the production of steam for the blowing engines. It is not a rich gas, the heating value being only about 93 B.t.u. per cu. ft., but its use improves the thermal efficiency of the blast furnace (page 266).

Coal Gas.—This is made by the dry distillation of coal in retorts. It is a somewhat expensive gas because only the volatile portion distills off, leaving a soft, noncoherent coke, which is valueless as a metallurgical coke. The coke may be used for making water gas or may be sold for domestic heating. Coal gas has a high heating value, being similar in composition to natural gas. It is used as a domestic fuel either alone or mixed with water gas. When mixed with water gas, the latter need not be carbureted.

By-product Coke-oven Gas.—The main object of a by-product coke plant is to produce high-grade metallurgical coke. The production of gas is of secondary importance, and its composition may vary considerably. Its fuel value is usually somewhat less than that of coal gas, but the composition is similar. If the coke plant is near a large city in which natural gas is not available, a portion of the coke-oven gas may be sold for domestic and industrial uses, producer gas being used for heating purposes around the mill. Otherwise it is used in the steel mill for heating open-hearth and reheating furnaces, soaking pits, or in boilers.

Oil Gas.—This is similar to coal gas in composition and is essentially the gas used in enriching carbureted water gas. Considerable quantities are made where oil is cheap and where coal or coke is expensive. Oil gas is made by passing a mixture of oil and steam through generators filled with checker-brick, after heating the brick by burning an air-oil spray.

Liquefied Petroleum Gases.—In 1937 about 142 million gallons of the gases propane, butane, and pentane from petroleum refineries were liquefied and sold as domestic fuel (29 per cent), as industrial fuel and in the manufacture of chemicals (50 per cent), as an internal-combustion engine fuel (12 per cent), and for gas enrichment and other uses (9 per cent). Propane is the principal constituent of the bottled gas used as a fuel.

PRINCIPLES OF COMBUSTION

The efficient use of a fuel involves providing the correct amount of air for combustion, heating to the ignition temperature, allowing the combustion to proceed in a properly designed furnace, and efficiently absorbing the heat produced in the equipment being heated. This section will be concerned with the general principles controlling the combustion process. The reader should consult books specializing on combustion and heat transfer for detailed information concerning the equipment involved.

In the burning of all fuels, the heat evolved is derived chiefly from carbon and hydrogen or their compounds. The sulfur contained in some fuels may burn and contribute to the heating value, but the quantity of heat thus derived is usually unimportant. In coke, practically all the carbon is present in the free state. In coal, a portion of the carbon is combined; in the gases, oils, and wood, it is all combined with other elements. Except in some of the gaseous fuels (Table 11), hydrogen is always combined, usually with carbon and oxygen.

Ignition Temperature (Kindling Temperature).—Everyone is familiar with the fact that fuels will exist in air practically indefinitely unless heated to a sufficiently high temperature to start active combustion. The temperature at which a substance ignites and continues to burn without further addition of heat is known as the kindling temperature or ignition temperature. This temperature is not very definite, since it is influenced by many factors such as the fineness of subdivision or amount of exposed surface if the com-

TABLE 11.—TYPICAL ANALYSES OF COMMON GASEOUS FUELS*

Gaseous fuel	Constituent, per cent by volume									B.t.u. per cu. ft. 60°F., 30 in. Hg, saturated H_2O		Theoretical flame temperature, °F.
	CH_4	C_2H_6	C_3H_8	C_2H_4	CO	CO_2	H_2	O_2	N_2	High or gross	Low or net	
Coal gas	34.0	....	....	6.6	9.0	1.1	47.0	...	2.3	634	560	3910
Coke-oven gas I	28.5	....	....	2.9	5.1	1.4	57.4	0.5	4.2	536	476	3430
Coke-oven gas II	33.9	....	....	5.2	6.1	2.6	47.9	0.6	3.7	600	538	3860
Blue water gas	....	....	....	....	43.4	3.5	51.8	...	1.3	310	285	4167
Carbureted water gas	14.8	....	....	12.8	33.9	1.5	35.2	...	1.8	578	529	4090
Oil gas	27.0	....	....	22.7	10.6	2.8	53.5	...	3.4	516	461	3970
Producer gas	2.6	....	....	0.4	22.0	5.7	10.5	...	58.8	136	128	3050
Blast-furnace gas†	....	....	....	....	26.2	13.0	3.2	...	57.6	93	91.6	2660
Natural gas I (Follansbee, W. Va.)	....	31.8	77.7	....	....	....	....	...	0.5	2,469	2,268	3840
Natural gas II (McKean County, Pa.)	32.3	67.0	....	....	....	....	....	...	0.7	1,482	1,350	3770
Natural gas III (Sandusky, Ohio)	83.5	12.5	....	....	....	0.2	....	...	3.8	1,047	946	3740

* HASLAM and RUSSELL, "Fuels and Their Combustion," p. 282, McGraw-Hill Book Company, Inc., New York, 1926.

† This is richer than most blast-furnace gases. For good practice the ratio CO/CO_2 lies between 1.5 and 1.7.

bustible is solid or liquid. In the case of gases the ignition temperature depends on

1. Pressure. The ignition temperature usually decreases somewhat with increase in pressure.

2. The ratio of combustible gas to air.

3. The size and shape of the vessel. The ignition temperature increases as the ratio of surface to volume of the vessel increases. The reason for this is easily seen, since to maintain combustion, the rate of heat evolution must be at least equal to the rate of heat loss from the vessel.

4. The presence of a catalyst, which may lower the ignition temperature.

Spontaneous Combustion.—The temperature attained during any exothermic chemical reaction is determined by the speed of the reaction and by the rate at which heat is removed by the surroundings. If oily rags, waste, or a fuel, such as coal, is stored in such a way that heat is only slowly dissipated, slow oxidation may produce sufficient heat to raise the temperature to the kindling temperature. Spontaneous combustion will then ensue.

Explosive Range. Limits of Inflammability.—The limiting composition of a gas-air mixture beyond which the mixture will not

TABLE 12.—LIMITS OF INFLAMMABILITY AT ORDINARY TEMPERATURES AND ATMOSPHERIC PRESSURES*

Gas	Limits expressed as per cent by volume of combustible gas in air	
	Lower limit	Upper limit
Hydrogen, H_2	6.2	71.4
Carbon monoxide, CO	16.3	71.2
Coal gas, coke-oven gas	7.	21.
Blue water gas	12.	67.
Blast-furnace gas	36.	65.
Methane, CH_4	5.8	13.3
Ethane, C_2H_6	3.3	10.6
Ethylene, C_2H_4	3.4	14.1
Ethyl alcohol, C_2H_5OH	3.7	13.7
Benzene, C_6H_6	1.4	5.5
Pentane, C_5H_{12}	1.3	4.9
Ether, $(C_2H_5)_2O$	1.6	7.7

* HASLAM and RUSSELL, "Fuels and Their Combustion," p. 265, McGraw-Hill Book Company, Inc., New York (1926).

ignite and continue to burn is called the explosive limit or limit of inflammability. For every combustible gas there exist two limits, the lower limit representing the smallest proportion, the upper limit the largest proportion of combustible gas that, when mixed with air, will sustain combustion.

In the determination of the explosive range, the temperature of the majority of the gas-air mixture is below the ignition temperature. Inflammation is started by supplying heat momentarily at a single point from an external source. Combustion will proceed only if the composition of the gas-air mixture lies between the upper and lower limits of inflammability. The limits of inflammability of gas-air mixtures are given in Table 12.

At pressures up to atmospheric pressure, the explosive range increases with increased pressure, the lower limit being decreased and the upper limit raised. Above atmospheric pressure, the upper explosive limits of most gases, CO and H_2 excepted, increase with increasing pressure. The lower limit for CO, H_2, and the saturated hydrocarbons up to pentane increases with increasing pressure above atmospheric pressure. Increase of temperature above ordinary atmospheric temperatures increases the explosive range, the lower limit being reduced and the upper limit raised.

The Mode of Combustion of Various Substances.—When two or more gases interact rapidly, with the evolution of more or less heat and light, the phenomenon is known as a flame. If little light is emitted (nonluminous flames), the reaction occurs between gaseous molecules. The majority of the light emitted from luminous flames is due to the presence of incandescent solid particles, which may be entrained in the gas stream or may be produced by the decomposition (cracking) of some of the compounds, usually hydrocarbons, in the burning gas. Although the combustion of liquids and many solids is accompanied by a flame, this is not due to the combustion of the solids and liquids themselves, but to the gases produced from them by the heat of the reaction. Energy is radiated from both luminous and nonluminous flames. The radiation from the latter lies mostly outside the visible spectrum, the majority of the energy, in both cases, being in the infrared region of the spectrum.

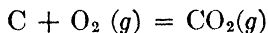
When an air-gas mixture is allowed to impinge upon a heated surface, it is found that combustion proceeds more rapidly on the surface than in the body of the gas. This is known as surface combustion, and the rate at which it proceeds is dependent on the temperature, the extent of the surface, and the speed with which

reactants can diffuse to the surface and the products of reaction away from it. If sufficiently hot, all surfaces show about the same effect in catalyzing the combustion reaction. At low temperatures some solids, *e.g.*, platinum or palladium sponge, are better catalysts than others.

The primary combustion reaction of solid fuels such as coke or charcoal, which do not vaporize, takes place on the surface of the solid. Such combustion is similar to the surface combustion of gases, except that only the oxygen of the air must diffuse to the surface, since the fuel, carbon, is already there.

Weight and Volume Relations in Combustion Reactions.—Combustion reactions, like all chemical reactions, obey the laws of conservation of matter and of energy. These laws may be stated as follows: neither matter nor energy is created or destroyed in chemical reactions. Since the atomic theory assigns the property of indestructibility of matter in chemical reactions to the atoms, the law of conservation of matter may be applied not only to the total amount of matter but also to each element involved in the reaction. The procedure of accounting for all the various kinds of matter that enter and leave a process is known as making a "material balance"; the corresponding procedure for energy is known as a "heat balance" or "energy balance." It is evident that these procedures are merely applications of the laws of conservation of matter and of energy. A simple example of a heat and material balance is given later in this chapter (page 74).

Since a correctly written or "balanced" chemical equation must also satisfy the law of conservation of matter, there must be the same number and kinds of atoms in the products of a reaction as there are in the reactants The starting point for any combustion calculation involving weight or volume is therefore a balanced chemical equation. Consider the equation



$$C + O_2\ (g) = CO_2(g)$$

This may be read, "One atom of carbon requires one molecule of oxygen gas to produce one molecule of carbon dioxide gas." Since the weight of an atom or molecule is so small, it is more convenient to use a larger unit, known as the "mole." The mole is defined as that weight of substance which is equal numerically to its molecular weight if the molecular weight is known; or to its formula weight if the molecular weight is unknown or without significance. With these definitions, the relation between the number of moles

of substance reacting will be the same as between the number of molecules reacting, and we may then read the above equation, "One mole of carbon requires one mole of oxygen gas to produce one mole of carbon dioxide gas."

The actual size of the mole will of course depend on the unit of weight used. In engineering work the convenient unit of weight is the pound, and the corresponding molar unit is the pound mole. In scientific work the gram is a convenient unit of weight and the corresponding molar unit is the gram mole (sometimes known as the gram molecular weight). The number of moles, $n = W/M$, where W is the weight and M the molecular or formula weight of the material.

The General Gas Equation.—All perfect gases obey the equation of state:

$$PV = nRT$$

where P = absolute pressure.
V = volume.
n = number of moles of gas.
R = the "gas constant."
T = absolute temperature.

Since nearly all actual gases and gaseous mixtures obey this equation within the accuracy of engineering measurements, except at high pressures or low temperatures, it will be found very convenient for combustion calculations. The value of the gas constant R is the same for all gases, but must of course be properly chosen to correspond with the units used in the general gas equation. The numerical values of R for various units in common use are given in Table 13.

Several useful relations may be deduced from the general gas equation. For example, if pressure and temperatures are held constant, it is seen that the volume is proportional to the number of moles. Applying this to reactions involving gases, Gay-Lussac's law of combining volumes is immediately obtained. This may be stated as follows: "At constant temperature and pressure, the volumes of reacting gases or gaseous reaction products are to each other as the coefficients in the balanced chemical equation representing the reaction."

As mentioned above, the gas law is obeyed by gaseous mixtures. We can then write

$$PV_1 = n_1RT \qquad (1)$$

for one constituent of a gas mixture and

$$PV = nRT \tag{2}$$

for the mixture as a whole, where $n = n_1 + n_2 + n_3 + \cdots =$ total moles of gases in the mixture. Dividing Eq. (1) by Eq. (2) and taking P and T constant, we obtain

$$\frac{V_1}{V} = \frac{n_1}{n} = N_1 = \text{mole fraction of constituent 1,} \tag{3}$$

which may be stated, "The fraction by volume of a constituent of a gaseous mixture (when the volume of the constituent is measured at the same temperature and pressure as the mixture) equals the mole fraction of the constituent in the mixture." The percentage by volume is 100 × the fraction by volume.

The partial pressure of a constituent of a gaseous mixture is defined as the pressure that the constituent would exert if present alone in the same volume and at the same temperature as the mixture. Proceeding as above, we can write

$$p_1V = n_1RT \tag{4}$$

where p_1 = partial pressure of constituent 1, and

$$PV = nRT, \tag{5}$$

where P is the total pressure on the mixture.

TABLE 13.—VALUES OF THE GAS CONSTANT R FOR VARIOUS UNITS

R	P	V	N	T
0.729	Atmospheres	Cubic feet	Pound moles	Degrees Rankine (°R = °F. + 460)
10.72	Pounds per square inch	Cubic feet	Pound moles	Degrees Rankine (°R. = °F. + 460)
1,544	Pounds per square foot	Cubic feet	Pound moles	Degrees Rankine (°R. = °F. + 460)
0.0821	Atmospheres	Liters	Gram moles	Degrees Kelvin (°K. = °C. + 273)

Dividing Eq. (4) by Eq. (5), we obtain

$$\frac{p_1}{P} = \frac{n_1}{n} = N_1 \qquad \text{or} \qquad p_1 = N_1P$$

This result may be stated, "The partial pressure of a constituent

of a gaseous mixture equals the mole fraction of the constituent multiplied by the total pressure on the mixture."

Another useful concept in working with gas mixtures is the mean molecular weight. If $n = n_1 + n_2 + n_3 + \cdots =$ total moles of gas in the mixture, the mean molecular weight $\bar{M}$ may be defined by the relation $\bar{M} = W/n$, where $W = W_1 + W_2 + W_3 + \cdots =$ the total weight of gas in the mixture. Substituting $W_1 = n_1M_1$; $W_2 = n_2M_2$, etc.,

$$\bar{M} = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \cdots}{n}$$

$$= N_1M_1 + N_2M_2 + N_3M_3 + \cdots$$

This relation is most useful if the analysis of the gas mixture is known in per cent by volume. Since the densities, or specific gravities, of gases are proportional to their molecular weights, the density ($\bar{d}$) of a gas mixture will be given by the equation $\bar{d} = N_1d_1 + N_2d_2 + N_3d_3 + \cdots$. If the weights of gases are known, it is more convenient to calculate $\bar{M}$ from the relation, $\frac{W}{\bar{M}} = \frac{W_1}{M_1} + \frac{W_2}{M_2} + \frac{W_3}{M_3} + \cdots$; obtained by substituting $n = \frac{W}{\bar{M}}$; $n_1 = \frac{W_1}{M_1}$ etc., in the relation $n = n_1 + n_2 + n_3 + \cdots$. The use of some of the relations discussed above may be conveniently illustrated by means of an example.

Example 1.—(*a*) Calculate the volume of oxygen and air required to burn 1,000 cu. ft. of ethane, C_2H_6, all gases being measured at 60°F. and 1 atm. pressure. (*b*) Calculate the volume of dry flue gases at 60°F. and 1 atm. when the theoretical air is used. (*c*) Calculate the volume of moist flue gases at 500°F. and 1 atm. pressure if 20 per cent excess air is used. The balanced equation for the reaction is $C_2H_6 + 3\frac{1}{2}\ O_2 = 2CO_2 + 3H_2O$.

(*a*) Using Gay-Lussac's law of combining volumes, the oxygen required is $1{,}000 \times 3\frac{1}{2} = 3{,}500$ cu. ft. at 60°F., 1 atm. Since air contains only 20.9 per cent of O_2, each mole of O_2 will be accompanied by 3.76 moles N_2; whence the theoretical air required is

$$4.76 \times 3{,}500 = 16{,}660 \text{ cu. ft. at } 60°\text{F., 1 atm.}$$

(*b*) The volume of CO_2 is $1{,}000 \times 2 = 2{,}000$ cu. ft. and of N_2 is

$$3.76 \times O_2 = 3.76 \times 3{,}500 = 13{,}160 \text{ cu. ft.}$$

The volume of dry flue gases at 60°F. and 1 atm. is the sum of these, or 15,160 cu. ft.

(*c*) To calculate the volume of moist flue gases at 500°F. and 1 atm., with 20 per cent excess air, it is most convenient to calculate first the volume at 60°F..

assuming that the water remains gaseous. From (*a*), the volume of oxygen required is 3,500 cu. ft. If 20 per cent of excess air is used, $0.20 \times 3{,}500 = 700$ cu. ft. of oxygen which will remain unconsumed in the flue gases. From (*b*) there will be $1.20 \times 13{,}160 = 15{,}790$ cu. ft. N_2 and 2,000 cu. ft. CO_2. The volume of water vapor is $3 \times 1{,}000 = 3{,}000$ cu. ft. Adding these, the total volume of combustion products is, at 60°F., 1 atm.,

$$V = V_{O_2} + V_{N_2} + V_{CO_2} + V_{H_2O} = 700 + 15{,}790 + 2{,}000 + 3{,}000$$
$$= 21{,}490 \text{ cu. ft.}$$

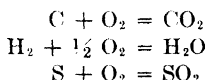
Making use of the gas equation, at constant pressure,

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}; \qquad V_2 = V_1 \cdot \frac{T_2}{T_1}$$

or

$$V_2 \text{ (vol. at 500°F.)} = 21{,}490 \times \frac{500 + 460}{60 + 460} = 21{,}490 \times \frac{960}{520} = 39{,}680 \text{ cu. ft.}$$

Example 2.—Calculate the theoretical volume of oxygen and of air required at 80°F. and 1 atm., for the combustion of 100 lb. coal whose composition is C = 69 per cent, H = 5.4 per cent, S = 1.0 per cent, N = 1.6 per cent, O = 15 per cent, ash = 8 per cent. The reactions involved are



$$C + O_2 = CO_2$$
$$H_2 + \tfrac{1}{2} O_2 = H_2O$$
$$S + O_2 = SO_2$$

	Per cent	Pound moles per 100 lb. coal	Moles O_2 required
C	69.	69/12 = 5.75	5.75
H	5.4	5.4/2 = 2.70	1.35
S	1.0	1/32 = 0.03	.03
N	1.6	1.6/28 = 0.05	
O	15.0	15/32 = 0.47	−0.47
			6.66

The volume of oxygen required is found by substituting in the gas equation. $V_{O_2} = nRT/P = 6.66 \times 0.729 \times (460 + 80) = 2{,}622$ cu. ft. and the volume of air is $4.76 \times V_{O_2} = 12{,}480$ cu. ft.

Heats of Combustion.—The heat of a reaction may be defined as the heat evolved when reaction takes place between the number of moles of reactants indicated by the chemical equation representing the reaction. If heat is evolved, the reaction is called "exothermic," if absorbed, "endothermic." A positive amount of heat appended to the chemical equation (Table 14) indicates heat evolved; a negative amount indicates the heat absorbed.

The heat of combustion is a particular kind of heat of reaction and may be defined as the heat evolved when one mole of a compound reacts with oxygen. In writing combustion reactions, it is always assumed that carbon is burned to carbon dioxide and hydrogen to water. Heats of combustion for the compounds that form an important part of most fuels are given in Table 14, along with additional heats of reaction for the important fuel-making reactions. As might be expected, the numerical value of the heat of combustion depends on the units used in expressing both the heat unit and the mole. Three sets of units are in common use: calories per gram mole, used in scientific work; centigrade heat units (c.h.u.) used by chemical engineers, and B.t.u. per pound mole, used by other engineers. The mean centigrade heat unit is one-hundredth of the amount of heat necessary to raise 1 lb. of water from 0 to 100°C. The conversion factors between these units are

Calories per gram mole = centigrade heat units per pound mole
Calories per gram mole × 1.8 = B.t.u. per pound mole

Unless otherwise noted, the heats of combustion given in this chapter are in B.t.u. per pound mole.

TABLE 14.—HEATS OF REACTION OF IMPORTANT COMBUSTION AND FUEL-MAKING REACTIONS

B.t.u. per pound mole*

$C + \frac{1}{2} O_2 = CO + 52{,}200$
$C + O_2 = CO_2 + 174{,}600$
$C + CO_2 = 2CO - 70{,}200$
$C + H_2O = CO + H_2 - 70{,}900$
$C + 2H_2O = CO_2 + 2H_2 - 71{,}600$
$CO + \frac{1}{2} O_2 = CO_2 + 122{,}400$
$CO + H_2O = CO_2 + H_2 - 700$
$H_2 + \frac{1}{2} O_2 = H_2O + 123{,}100$
$CH_4 = C + 2H_2 - 36{,}800$
$CH_4 + 2 O_2 = CO_2 + 2H_2O + 384{,}000$
$C_2H_4 = 2C + 2H_2 + 27{,}000$
$C_2H_4 + 3 O_2 = 2CO_2 + 2H_2O + 622{,}400$
$C_2H_2 + 2\frac{1}{2} O_2 = 2CO_2 + H_2O + 562{,}000$
$C_2H_6 + 3\frac{1}{2} O_2 = 2CO_2 + 3H_2O + 668{,}300$
$C_3H_8 + 5 O_2 = 3CO_2 + 4H_2O + 952{,}000$
$C_4H_{10} + 6\frac{1}{2} O_2 = 4CO_2 + 5H_2O + 1{,}237{,}000$
$C_6H_6 + 7\frac{1}{2} O_2 = 6CO_2 + 3H_2O + 1{,}413{,}000$

* HASLAM and RUSSELL, "Fuels and Their Combustion," pp. 140, 205, McGraw-Hill Book Company, Inc., New York (1926). The above values assume reactants and products at 60°F. and water in the liquid state. For the combustion reactions, they are termed high (or gross) heats of combustion. To secure low (or net) heats of combustion deduct 19,000 B.t.u. per mole of water formed.

Since the heat of a reaction varies with the temperature, as will be discussed later on, it is important to specify the temperature and physical state of reactants and products in any table of heats of reaction. In Table 14, the heats of reaction given assume that the reactants and products are at 60°F. and that water is in the liquid state. These values, and also those given previously in the discussion of solid and liquid fuels, represent the heat of combustion as it would be determined in a calorimeter, in which the products of combustion are cooled to a temperature only slightly above that of the reactants. In practice, the products of combustion practically always escape from the process at a higher temperature than the boiling point of water. The heat liberated when water vapor is condensed to liquid water is therefore never available. For this reason, it is customary to distinguish between the heat of combustion as determined in a calorimeter, known as the "gross" or "high" value, and the value one would obtain were the water to remain in the gaseous state, known as the "low" or "net" value. The low or net value of the heat of combustion is

TABLE 15.—CALCULATION OF THE HEATING VALUE OF A PRODUCER GAS

Constituents	(1) (Dry) %	(2) Mole fraction	(3) Moles per cu. ft. at 30 in. Hg, 60°F., saturated with H_2O × 1,000	(4) Heat evolved by each constituent
CH_4	2.6	0.026	0.0676	25.9
C_2H_4	0.4	0.004	0.0104	6.5
CO	22.0	0.220	0.5716	70.0
CO_2	5.7	0.057	0.1481	0.0
H_2	10.5	0.105	0.2728	33.6
N_2	58.8	0.588	1.5276	0.0
Gross heating value of gas B.t.u. per cu. ft. at 60°F., 30 in. Hg, saturated with H_2O.				136.0

easily calculated from the high or gross value by deducting from the latter 19,000 B.t.u. per pound mole of water formed in the reaction. When the heating value of a fuel is given in B.t.u. per pound, the net value may be calculated by subtracting 19,000/18 or 1056 B.t.u. per lb. of water formed.

In the solid and liquid fuels, the exact nature and proportions of the various compounds existing in the fuel are usually unknown,

and it is therefore impossible to calculate the heating value of the fuel with high precision. Approximate values may be obtained by the use of empirical formulas as discussed on pages 38 to 52. To secure precise values the fuels must be burned in a calorimeter. Precise values of the heating value of gaseous fuels may be obtained either by measuring the heat of combustion in a flow-type calorimeter, such as the Junkers, or by calculation from the gas analysis. An example of this type of calculation will now be given, using the producer-gas analysis given in Table 11. The calculations are summarized in Table 15.

Explanation.—Column (2) is calculated from column 1 by dividing by 100. Column (3) is calculated by multiplying the moles of dry gas in 1 cu. ft. at 30 in. Hg and saturated with water vapor by the respective mole fractions in column (2). The moles of dry gas under these conditions are calculated as follows: The partial pressure of dry gas,

$$p = 30 - \text{vapor pressure of water at } 60°\text{F.}$$
$$= 30 - 0.53 = 29.47 \text{ in. Hg}$$

Since one standard atmosphere = 29.92 in. Hg,

$$p = \frac{29.47}{29.92} = 0.985 \text{ atm.}$$

Solving the gas equation for n and substituting therein,

$$n = \frac{PV}{RT} = \frac{0.985 \times 1}{0.729 \times (460 + 60)} = 2.598 \cdot 10^{-3}$$

Column (4) is calculated by multiplying the figures of column (3) by the appropriate heat of combustion from Table 14.

Heat of Combustion and Temperature.—As previously mentioned, the heat of combustion depends upon the temperature, a fact which at first sight would appear to make combustion calculations very complicated. Examination of the problem shows that this is not the case. We usually know that fuel and air enter the process at one temperature and that the products of combustion leave at some higher temperature. The law of conservation of energy then assures us that the heat evolved in the process depends only on the initial and final conditions, and not upon how the process is carried out. The maximum heat available to the process is then the sensible heat in the entering fuel and air, plus the heat of combustion, less the heat carried out in the stack gases. In order to calculate the first and last of these quantities, it is necessary

to know the specific heats or heat capacities of the substances involved.

Specific Heats and Heat Capacity.—Since nearly all combustion calculations are made at pressures near one atmosphere, we shall discuss only the specific heat and heat capacity at constant pressure. A textbook on physical chemistry should be consulted for a discussion of heat capacities at constant volume and the effect of pressure on heat capacities.

In scientific work, the specific heat is defined as the amount of heat necessary to raise the temperature of unit weight of substance one degree, the measurement being made at a given temperature. In engineering work it is usually more convenient to use the "mean specific heat," which is the amount of heat necessary to raise the temperature of unit weight of a substance from a given base temperature (either 32 or 60°F.) to a higher temperature, divided by the temperature rise.

The "mean molal heat capacity," $\bar{C}_p$, is the heat necessary to raise the temperature of one mole of substance from a given base temperature to a higher temperature, divided by the temperature rise.

The units of specific heat are B.t.u. per pound degree fahrenheit, or calories per gram degree centigrade, these quantities being numerically equal for a given substance. Specific heat × molecular weight = molal heat capacity.

Heat Capacities of Gases.—The molal heat capacities of common gases are shown graphically in Fig. 6.

The molal heat capacity of a gaseous mixture may be calculated from the heat capacities of the pure gases in the mixture by the equation: $\bar{C}_p$ (mixture) $= \bar{C}_{p_1}N_1 + \bar{C}_{p_2}N_2 + \bar{C}_{p_3}N_3 + \cdots$; where $\bar{C}_{p_1}$, $\bar{C}_{p_2}$, $\bar{C}_{p_3}$, etc., are the mean molal heat capacities of the pure gases and N_1, N_2, N_3, etc., are their mole fractions.

Heat Capacities of Solids and Liquids.—For accurate values of the heat capacities of solids and liquids, a good handbook should be consulted. No generalizations can be given on the heat capacities of liquids, but approximate values for the heat capacities of solids may be secured from (1) the rule of DuLong and Petit, which states that for the solid elements with atomic weights greater than potassium, $C_p = 6.2$ B.t.u. per lb. mole °F. (approximately), and (2) Kopp's rule for solid compounds. According to the latter rule, C_p for a solid compound is obtained by adding the atomic heat capacities of the constituent elements, using the DuLong and Petit value of 6.2 for the heavier elements and for the lighter

elements the following values: O, 4.0; H, 2.3; C, 1.8; S, 5.4; B, 2.7; F, 5.0; Si, 3.8; P, 5.4. Using this rule, the molal heat capacity of silver phosphate, Ag_3PO_4, would be $3 \times 6.2 + 5.4 + 4 \times 4.0 = 36.0$ B.t.u. per lb. mole°F.

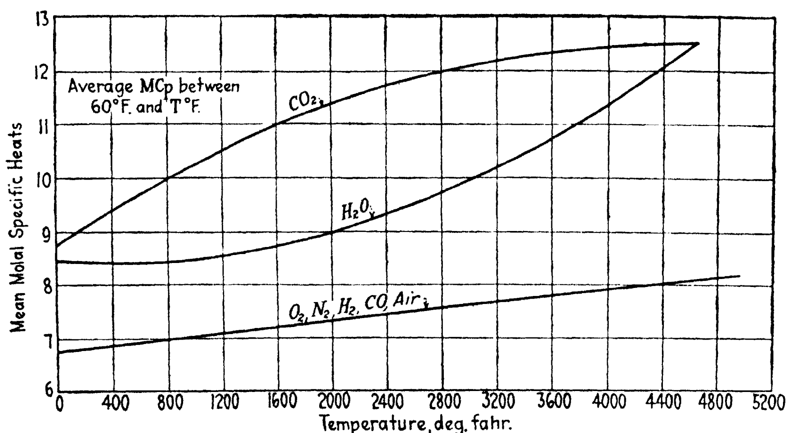


FIG. 6.—Mean molal heat capacities of gases between 60°F. and t°F. (*From Haslam and Russell, "Fuels and Their Combustion."*)

Sensible Heat, Latent Heat, Total Heat, and Potential Heat.—The *sensible heat* of a material at the temperature T is defined as the heat content of the material at temperature T less the heat content at some selected base temperature T_0, excluding the heat of any phase changes that may occur. Since we have chosen 60°F. as the base temperature for heats of combustion, it is convenient to choose the same base temperature for calculating sensible heat.

$$\text{Sensible heat} = n \times C_p \times (T - T_0)$$
$$= W \times (\text{sp. heat}) \times (T - T_0)$$

The *latent heat of fusion* (often called merely the heat of fusion) is the heat required to melt or fuse one mole of material at constant temperature (usually the melting point). The *latent heat of vaporization* is the heat required to vaporize one mole of material at constant temperature. The *total heat* is the sum of the latent heats and the sensible heat. *Potential heat* or *unused heat* is the heat of combustion of unburned fuel or of products of combustion that have not been oxidized to the state assumed in writing the combustion reactions.

Heat and Material Balance.—All the concepts necessary for making heat and material balances have now been defined and discussed. As previously mentioned, the material balance may

be applied both to the total material and to each element entering and leaving a process. When complete sets of data are available on a process, the heat and material balances may be used to check the accuracy of measurement. If complete data are not available, the balances are valuable for calculating the missing data. The heat and material balances are almost imperative in studies to improve a process or to trace losses of energy and material.

Heat and material balances are made simultaneously, since the material balance is necessary in order to make the heat balance. The total heat input to the process must equal the total heat output. The following items must be considered under each of the headings:

I. Total heat input,
   a. Heat of combustion of fuel.
   b. Sensible and latent heat in fuel, air, and other raw materials.
   c. Heat from exothermic reactions in the process.

II. Total heat output,
   a. Sensible and latent heat in the product.
   b. Heat absorbed by endothermic reactions in the process.
   c. Potential, sensible, and latent heat in the combustion products (ash and flue gases).
   d. Heat losses to the surroundings by radiation, convection, etc.

Example.—Heat balance of a boiler using coal as fuel and generating steam.

Data: Coal used .... 4,980 lb. per hr.
Water fed .... 41,400 lb. per hr.
Feed-water temperature .... 202°F.
Steam temperature .... 564°F.
Steam pressure .... 245 psi gauge
Flue gas temperature .... 700°F.

Coal Analysis,	Per Cent by Weight	Flue Gas Analysis,	Per Cent by Volume	Cinder,	Per Cent by Weight
C	76.3	CO_2	13.0	C	28.5
H	4.8	O_2	5.7	Ash	71.5
O	4.0	CO	0.6		100.0
N	0.6	N_2	80.7		
S	1.2		100.0		
Ash	9.7				
H_2O	3.4				
	100.0				

B.t.u. per pound = 13,400.

I. *Total heat input per hour.*

a. Heat of combustion of coal:

(Weight of coal) × (B.t.u. per lb.)

4,980 × 13,400 = 66,730,000 B.t.u.

b. Sensible heat in feed water:

(Weight of water) × (temperature above base) × (specific heat)

41,400 × (202 − 60) × 1 = 5,879,000 B.t.u.

Total heat input per hour = 72,609,000 B.t.u.

II. *Total heat output per hour.*

a. Heat in steam: From steam tables, the total heat in steam at 245 psi gauge and 405°F., using 32°F. as the base temperature, is 1,294,7 B.t.u. per lb. Since our base temperature is 60°F., we must subtract 60 − 32 = 28 B.t.u. from this value, leaving 1,266.7 B.t.u. per lb. of steam.

(Weight of steam) × (B.t.u. per lb.)

41,400 × 1,266.7 = 52,437,000 B.t.u.

b. Potential heat due to carbon in cinder:

(Weight of coal)	×	(lb. ash per lb. coal)	= (weight ash)
4,980	×	0.097	= 483 lb.
(Weight of cinder)	×	(lb. carbon per lb. cinder)	= (carbon in cinder)
$483 \times \frac{100}{71.5}$	×	0.285	= 193
(Carbon in cinder)	×	(B.t.u. per lb. carbon)	
193	×	15,544	= 2,807,000 B.t.u.

c. Heat loss in stack gases:

(Carbon in coal) − (carbon in cinders) = (carbon in stack gases)

4,980 × 0.763 − 193 = 3,607

$\frac{3,607}{12}$ = 301 moles C in stack gases = moles CO + moles CO_2

From flue gas analysis, the total CO_2 and CO is 13.0 + 0.6 = 13.6 per cent.

$\frac{301}{0.136}$ = 2,210 moles of dry stack gases.

(Moles of dry gases)	×	(mole fraction)	
2,210	×	0.130	= 287 moles CO_2
2,210	×	0.870	= 1,923 moles O_2, N_2, CO

(O_2, N_2, and CO are lumped together since their heat capacities are equal.)

Sensible heat per pound mole of dry gases at 700°F.

= C_p × (700 − 60) = 6300 B.t.u. per mole of CO_2, 4,450 B.t.u. per mole of O_2, N_2, and CO and 5400 B.t.u. per mole of H_2O.

(Moles) × (B.t.u. per mole)

Sensible heat in CO_2 = 287 × 6,300 = 1,808,000 B.t.u.

Sensible heat in O_2, N_2, and CO = 1,923 × 4,450 = 8,557,000 B.t.u.

Sensible heat in dry stack gases = 10,365,000 B.t.u.

Heat in water from moisture and hydrogen in coal:

Moisture in coal = 4,980 × 0.034 = 169 lb.

Water from H in coal = 4,980 × 0.048 × $^{18}/_{2}$ = 2,150 lb.

Total moisture in stack gases, neglecting moisture in air = 2,319 lb.

Sensible heat in $H_2O = \frac{2,319}{18} \times 5,400 = 697,000$

Latent heat in $H_2O = \frac{2,319}{18} \times 19,000 = \underline{2,455,000}$

Total heat in H_2O in stack gases = 3,152,000

d. Potential heat in stack gases:

(Moles dry stack gases) × (mole fraction)

2,210 × 0.006 = 13.3 moles CO

(Moles CO) × (B.t.u. per mole)

13.3 × 122,400 = 1,628,000 B.t.u.

Total stack losses = 15,145,000 B.t.u.

Summary of Heat Balance

Input	B.t.u.	%	Output	B.t.u.	%
Heat in coal	66,730,000	91.9	Heat in steam	52,437,000	72.2
Heat in feed water	5,879,000	8.1	Heat in cinders	2,807,000	3.9
			Stack loss	15,145,000	20.9
Total	72,609,000	100.0	Radiation, etc.	2,220,000	3.0
			Total	72,609,000	100.0

Calorific Intensity. Theoretical Flame Temperature.—The temperature attainable in flames is a very important quantity. When heat is converted into work, as in an internal-combustion engine, the maximum possible efficiency (Carnot-cycle efficiency) is given by the formula $\frac{T_2 - T_1}{T_2}$; where T_2 is the highest temperature attained (*i.e.*, the flame temperature) and T_1 is the exhaust temperature. The flame temperature represents the maximum temperature to which an object can be heated by the flame. Fur thermore, the rate of heating an object increases as the difference in temperature between flame and object increases.

It is difficult to measure, or even to calculate, the actual temperature of a flame with any degree of accuracy. Because of this difficulty, "theoretical flame temperatures" are calculated on the assumption that combustion takes place instantly, completely, and without loss of heat to the surroundings. In other words, all the heat of combustion is assumed to heat the gaseous products of combustion. Actual flame temperatures will always be less than theoretical flame temperatures, since none of the assumptions made in calculating the latter are realized. Nevertheless, the actual flame temperatures of different fuel gases will be in the same order

as the theoretical flame temperatures, and can therefore be used for comparing different fuels. Theoretical flame temperatures may be calculated by the formula:

$$\text{Theoretical flame temperature} = \frac{(\text{heat of combustion} + \text{sensible heat in fuel and air})}{(\text{total quantity of combustion products}) \times (\text{their mean specific heats})}$$

The theoretical flame temperatures given in Table 11 are calculated on the assumption that fuel and air enter the flame at 60°F. and the theoretical air is used. The heat of combustion used is the low or net value, since the water produced is in the vapor state. Theoretical flame temperatures are most easily calculated by trial and error as follows: A temperature is first assumed. The mean specific heats are determined for this temperature and substituted in the foregoing equation after evaluating the other needed quantities, as previously described. Solution of the equation gives a new temperature. The theoretical flame temperature will lie between the assumed temperature and that calculated from the formula. A new temperature is assumed between these two, and the process repeated until the assumed and calculated temperatures agree. The temperature thus found is the theoretical flame temperature.

Effect of Excess Air.—If it were possible to burn a fuel completely with the theoretical amount of air, the maximum possible efficiency would be obtained. Under actual conditions, considerable potential heat is lost when the theoretical air is used, and trouble is experienced with many fuels due to smoke. As excess air is supplied, the loss of sensible heat in the stack gases increases, due both to the greater quantity of stack gases and to their higher temperature. The optimum amount of excess air depends upon the design of the furnace, the fuel used, and the equipment used to burn it. For a given furnace, the optimum excess air is that which makes the sum of the potential heat loss and the sensible heat in the stack gases a minimum. If for other reasons the optimum air must be exceeded, the amount of air over the optimum should be kept as low as possible.

OUTLINE OF PETROLEUM REFINING

Many of the liquid fuels discussed in earlier sections of this chapter and most of the lubricants discussed in the following section are derived from crude petroleum by various refinery processes.

It seems desirable therefore to give a brief outline of the methods whereby these important engineering materials are produced.

The Constitution of Petroleum.—Petroleum, crude oil, is essentially a solution of gaseous and solid hydrocarbons in a mixture of liquid hydrocarbons. The term "petroleum" is derived from two words, *petra* and *oleum* meaning "rock oil" or "mineral oil." Most crude oils also contain small amounts of sulfur, nitrogen, and oxygen. The amount of sulfur is usually less than 1 per cent and rarely exceeds 3 per cent. The amounts of nitrogen and oxygen are exceedingly small. Three types of hydrocarbons[1]—paraffins, naphthenes, and aromatics—constitute most of the hydrocarbons present in petroleum. In all but a few crude oils, the percentage of aromatics is comparatively small. The absence of low-molecular-weight, unsaturated hydrocarbons in petroleum is significant because it indicates that petroleum was not formed by destructive distillation or other high-temperature reactions. It is most generally believed that petroleum was formed by the decomposition in low-temperature reactions (bacterial action, fermentation, etc.) of plant and animal remains laid down in past geological ages.

Crude petroleums are usually classified as to "base," which is determined by the character of the hydrocarbons present in the crude. *Paraffin base* crudes consist principally of paraffin hydrocarbons, *naphthene* or *asphalt base* crudes have naphthenic hydrocarbons as their main constituents, and *mixed base* crudes contain each of these types of hydrocarbons. Crude oils from a few of the producing regions contain fairly high concentrations of aromatic hydrocarbons and are called *aromatic base* crudes. Crude oils from no two producing fields are alike. They vary from pale, straw-colored, mobile, transparent liquids up to dark, viscous, nontransparent crudes. Most crude oils have specific gravities in the range from 0.850 to 0.940, although some heavy crudes possess values as high as 1.06.

Petroleum Production.—The first oil well was dug at Titusville, Pa. in 1859. Since that time the industry has grown by leaps and bounds and oil fields have been discovered and developed in many localities all over the world. In 1937, the world production of petroleum amounted to slightly over 2 billion barrels (42 gal. each),

[1] See McCutcheon, Seltz, and Warner, "General Chemistry," 3d ed., pp. 554–561, D. Van Nostrand Company, Inc., New York (1939), or any of the standard textbooks of organic chemistry.

with 62.75 per cent of this being produced in the United States. The principal oil-producing regions and the relative importance of each region are indicated in Table 16.

TABLE 16.—CRUDE OIL PRODUCTION (1937)

Country or region	Per cent		Millions of bbls.	
United States		62.75		1,276
Texas (except Gulf Coast)	19.42		395	
California	11.72		238	
Oklahoma	11.24		229	
Gulf Coast	8.70		177	
Kansas	3.48		70	
New Mexico	1.89		38	
Appalachian	1.67		34	
Others (U. S.)	4.63		95	
Europe		12.70		259
Russia	9.69		197	
Rumania	2.61		53	
Others (Europe)	0.40		9	
South America		12.67		258
Venezuela	9.18		187	
Others (S. A.)	3.49		71	
Asia		6.54		133
Iran	3.81		78	
Iraq	1.58		32	
Others (Asia)	1.05		23	
East Indies		2.88		59
Mexico		2.30		47
Others		0.16		

Although some oil fields were discovered entirely by accident, present-day prospecting employs carefully designed geological and geophysical methods.[1]

Principal Products from Crude Oil.—Gasoline, gas and fuel oil, kerosene, and lubricants are the most important products obtained from crude oil. In addition, roughly 10 per cent of the crude reaches the market in the form of a great variety of minor products: paraffin wax, petrolatum (petroleum jelly or Vaseline), medicinal mineral oil, dry-cleaners' naphtha, solvents and thinners for paints, varnishes, lacquers, and enamels, petroleum coke, lamp- or gas black, solvents and spreaders for insecticides and fungicides,

[1] DEGOLYER (editor), "Elements of the Petroleum Industry," pp. 21–89, A.I.M.E., New York (1940).

finely divided sulfur; ethylene, propylene, and cyclopropane as general anesthetics; asphalts, road tars, and a host of other products. Moreover, there is a rapidly growing chemical industry based upon the use of petroleum hydrocarbons as raw materials to produce synthetic rubber, plastics, resins, alcohols, glycols, glycerol, ethers, amines, and a great variety of organic chemicals.

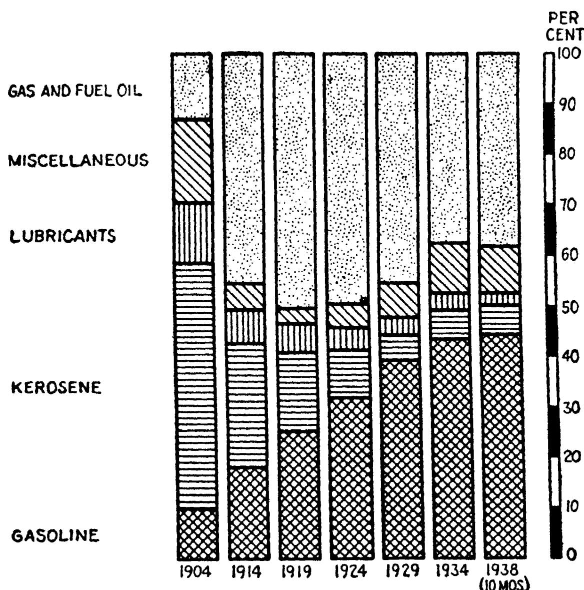


Fig. 7.—Principal products from crude oil. (*From "Elements of the Petroleum Industry," A.I.M.E., New York,* 1940.)

In the early years of the industry, kerosene was the most valuable petroleum product, but in recent years the demand for it has been relatively small. The rapid development of the automobile, aircraft, and machine industries has enormously increased the demand for motor fuels and lubricants. As a consequence, refinery practice today places the emphasis upon obtaining the maximum yields of gasoline and lubricating oil consistent with economy of operation. Changes in the relative importance of the principal products from crude oil since 1904 are indicated in Fig. 7.

Refinery Practice.—The petroleum industry was started by men without scientific or technical training. As a consequence, the early refining methods were comparatively crude and the art made slow progress by the empirical method of trial and error. During the last twenty years, however, the industry has been

revolutionized as a result of chemical research and the application of the methods of modern chemical engineering to operations. As a result, refinery practice has been greatly improved and made more flexible. Today, refinery practice may be readily adapted to the properties of the available crude oils and to the condition of the market for various petroleum products. As it would be impossible here to describe the actual present practice in even the most important refineries, a very general outline must suffice.

Distillation is, as it always has been, the most important processing step in petroleum refining. However, many of the unit operations of chemical engineering are utilized in the design and operation of a modern refinery: heat transfer, fluid flow, extraction, filtration, centrifugal separation, agitation, and catalysis being the most important. Modern refinery processes also are characterized by a high degree of automatic control of pressures, temperatures, and rates of flow.

The distillations carried out in a modern refinery may be divided into three groups: (1) normal-temperature and ordinary-pressure distillations, usually called "skimming" or "topping." This is usually the first operation in refining a crude oil. (2) High-temperature—high-pressure distillation with the objective of accomplishing "cracking" to make gasoline and other more volatile products from the heavier fractions of crude oil. (3) Vacuum distillation at subnormal temperatures to prevent "cracking" of heavier materials such as lubricating oils. In all these processes, the entering oil is preheated by passing through heat exchangers in which heat is transferred to the material from hot outgoing vapors or residual fractions. From the heat exchangers, the oil flows through tubes properly placed in a "pipe-" or "tubular still" furnace where it is heated to the proper distillation temperature. The heated stream of oil from the furnace tubes flows to a fractionating tower which usually is of the "bubble plate" type such as is illustrated in Fig. 8. Vapors formed from the heated oil stream escape up through the bubble plates while the unvaporized residue moves down and is withdrawn from the bottom. Bubble plates are among the most efficient large-scale fractionating devices known; all vapors passing up through the column must bubble through pools of liquid maintained on each plate. In the upper part of the tower the temperature is lowered by the controlled introduction of cold "reflux" oil or other means, resulting in the condensation of the higher boiling constituents of the vapor and controlling

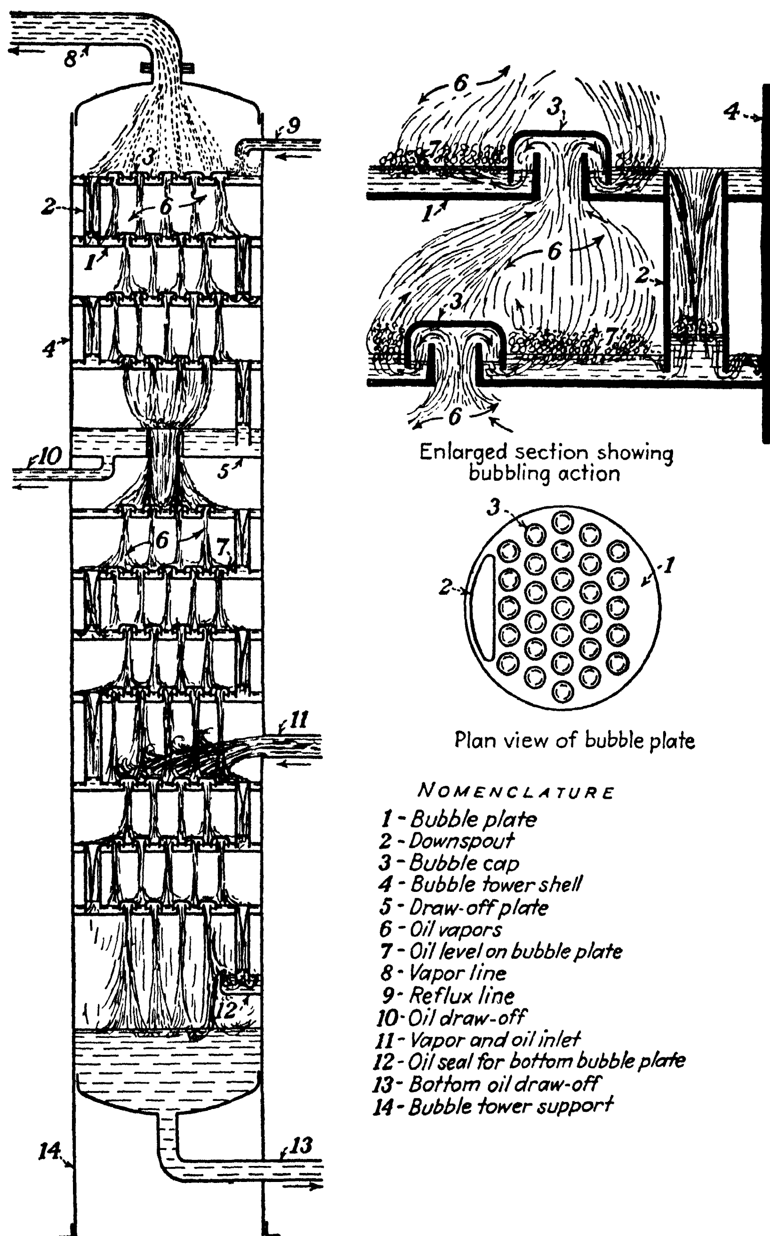


FIG. 8.—Bubble-plate fractionating tower. (*From "Elements of the Petroleum Industry," A.I.M.E.. New York,* 1940.)

the boiling range (volatility) of the fraction recovered from the top of the tower.

The size, number of plates, and other features in the design of the bubble tower will depend upon the separations that are to be accomplished and the desired capacity. For example, a bubble tower to be adequate for "topping" or "skimming" 10,000 bbl. of average crude oil per day would need to be about 10 ft. in diameter, 60 ft. high, and equipped with between 25 and 30 bubble plates.

Continuous "Skimming" or "Topping" of Crude Oil.—In a typical continuous skimming operation, crude oil preheated in a

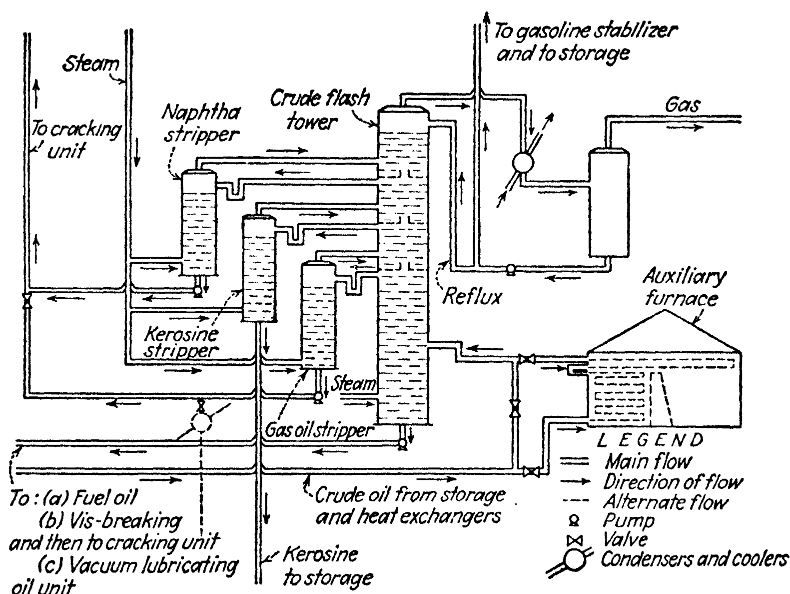


FIG. 9.—A typical skimming or topping unit.

heat exchanger flows through a pipe still where it is heated to approximately 550°F. (290°C.) and then to a bubble tower from which gas and gasoline are obtained as overhead products. In order of decreasing volatility, naphtha, kerosene, and gas oil fractions are taken from the proper progressively lower levels of the tower as side streams. As indicated in Fig. 9, all these fractions pass through "strippers," a portion of each being returned to the bubble tower as reflux. The heavy, least volatile portion of the crude oil leaves the bottom of the bubble tower in a continuous stream.

The overhead gasoline fraction (straight-run gasoline) after being put through a gasoline stabilizer may go to storage, or may be "reformed" (page 89) or blended to improve its octane rating. A goodly portion of the naphtha and kerosene fractions are marketed as such after treatment (page 91) and some gas oil is sold as a light fuel oil, but ordinarily the bulk of the heavy gas oil is sent to cracking units for the production of more gasoline. The heavy oil from the bottom of the skimming unit bubble tower may be used in a variety of ways: (1) It may be utilized directly as fuel oil. (2) It may be sent through as a "vis-breaking" unit (page 88) and then through a cracking unit for the production of more gasoline. (3) It may be utilized to produce lubricating oils and various by-products.

Cracking.—Although there were only four automobiles in the United States in 1895, the number had increased to over a million in 1913, to 10 million in 1921, and to 20 million in 1927. Furthermore, owing to the improved quality of both highways and automobiles, the average yearly mileage per automobile had greatly increased. By 1913, the consequent tremendous increase in gasoline consumption made "cracking" an important process in the petroleum industry to increase the yield of motor fuel from crude oil. Cracking consists in subjecting the heavier, less volatile fractions of crude oil, such as gas oil and fuel oil, to such conditions, usually high temperature and high pressure, that they will be destructively distilled to produce lighter, more volatile hydrocarbons. Owing to the development of cracking and other improvements, the yield of gasoline has been increased from 10 or 12 per cent to the present average of about 45 per cent of the crude oil. Cracking contributes approximately half of the present gasoline production.

For an account of the development of cracking processes from the first commercially successful one devised by Burton to the present-day more efficient ones, the reader must consult other references.[1] Available space permits only a brief discussion of present practice. Today, the refiner will, on a basis of an economic balance, utilize one of three general methods of cracking:

1. Thermal cracking:
   a. Liquid phase.
   b. Gas phase.

[1] KALICHEVSKY and STAGNER, "Chemical Refining of Petroleum," Reinhold Publishing Corporation, New York (1933).

2. Catalytic cracking.
3. Hydrogenation cracking.

Thermal processes account for the bulk of cracking at present, but catalytic cracking is growing in importance and several large units already are in operation. Hydrogenation cracking, although not now economical for gasoline production, has found some specialized uses in refineries and must be considered as a possibility for future use, especially when our supply of crude oil begins to decline.

Thermal Cracking.—The most commonly used process for thermal cracking is the so-called liquid-phase process. Actually it is a combination of the liquid- and vapor-phase processes because a part of the charge usually is vaporized before it enters the true cracking section of the coil. The material to be cracked enters pipe stills operating in the temperature range from 850 to 1000°F. (450 to 540°C.) under pressure of from 200 to 900 psi. The incoming stock is thus converted into a sort of synthetic crude with most of the carbon formed being carried along in the stream. The cracked material enters a bubble tower in which gasoline is taken off as an overhead product. Light and heavy gas-oil fractions are taken off as side streams and a heavy residuum leaves the bottom of the tower. The gas-oil fractions are continuously returned to the cracking coil so that the principal products from the cracking unit are cracked gasoline and a heavy residuum suitable for fuel oil. As minor necessary (but undesirable) by-products, some gas and coke are obtained. A typical thermal cracking unit operating on good quality gas oil will produce approximately 65 per cent of gasoline having an octane number of 66 to 70, about 25 per cent of residual fuel oil, 9 to 10 per cent of gas, and 1 per cent or less of coke.

The invariable production of heavy residual oil along with gasoline in thermal cracking shows that some of the active fragments produced by cracking unite in a process known as polymerization to produce molecules even larger than those in the material charged into the cracking unit. To satisfy the demand for petroleum coke, a small amount of the heavy residual oil is further destructively distilled to dryness in batch stills. Petroleum coke is essentially ash free and is widely used for making artificial graphite furnace electrodes and other graphite and carbon articles.

In true vapor-phase thermal cracking, all of the material to be cracked is vaporized in pipe stills and the vapors subjected to higher temperatures (1000 to 1050°F.) but lower pressures (25 to 50 lb.) than in liquid-phase cracking. Higher octane gasoline may be made

by this method but the high percentage of gas produced is a decided handicap, preventing the wide-spread use of the vapor-phase process.

Catalytic Cracking.—Recently, the cracking of heavy petroleum fractions into gasoline by catalytic processes has attained commerical importance. There are two important processes which have been, or seem certain to be, developed on a large scale commercially: (1) the Houdry or "fixed-catalyst-bed" process and (2) the "moving-catalyst-bed" process. The development of each of these processes is supported by its group of major oil companies.

In the Houdry[1] process, the material to be cracked is vaporized in pipe stills and the vapors are led to towers, much like bubble towers in outward appearances, where they are brought into intimate contact with beds of a suitable catalyst, such as synthetic clays promoted with zirconium oxide. The present installations are operated at temperatures in the range 800 to 900°F. (430 to 480°C.) and at pressures from 15 to 50 psi. From the catalyst towers, the cracked product goes to bubble towers where 35 to 45 per cent yields of 78- to 80-octane gasoline are obtained. Gas, to the extent of 4 to 6 per cent of the charge, and 37 to 47 per cent of a gas oil also are produced. Carbon equal to from 2 to 4 per cent of the charge is deposited on the catalyst which decreases its activity at such a rate that it must be regenerated after 8 to 10 min. During the time required for regenerating the catalyst by burning off the carbon, the vapor stream is automatically transferred to another catalyst tower. This process produces no heavy residuum such as is obtained in thermal cracking, the residuum being more like gas oil although somewhat heavier than the charging stock. It can be catalytically cracked by recycling, but it seems to be more economical to subject it to thermal cracking or to use it as diesel fuel or furnace oil. The facts indicate that catalytic cracking, followed by thermal cracking of the residuum, will produce 2 to 5 per cent more of 5 to 6 higher octane number gasoline than would be obtained from all-thermal cracking.

The "moving-catalyst-bed" process uses the catalyst in the form of a fine powder which, injected with the gas-oil vapors in the reactor chamber, moves upward slowly with the vapors. The combined stream is led from the top of the chamber to a cyclone-type separator and the catalyst-free vapors proceed to the usual frac-

[1] Houdry, Burt, Pew, and Peters, *Proc. 19th Ann. Meeting, Am. Petroleum Inst.*, **19**, Sec. III (1938).

tionating tower. The separated catalyst is returned to a regenerator unit where the carbon is burned off and its activity is restored for re-use. In pilot plant operation, processing 100 bbl. per day, this catalytic process shows good yields of high-octane gasoline. Larger plants have been under construction and may now be in operation, but performance data are not yet available.

It seems certain that these two processes for catalytic cracking will find a place of importance in the petroleum industry.

Combination Units.—When the principal object is to produce as much gasoline as possible from crude oil, one frequently finds so-called "combination units" operated by refineries.[1] In these units, crude oil is first put through a skimming operation such as has already been described. The residual oil from the skimming operation and the heavy oil from the cracking unit are put through a "vis-breaking" unit which consists of a pipe still heater and a combined evaporator and bubble tower. The "vis-breaking" operation is a mild thermal cracking step, which produces a small amount of gasoline and a residual heavy fuel oil; but its principal product is a gas-oil cracking stock which is supplied to the high-pressure cracking unit. The continuous operation of a combination unit represents a marvel of modern instrumentation and automatic control.

Hydrogenation Cracking.—When heavy oils are subjected to high temperatures and pressures in the presence of hydrogen and a suitable catalyst, the oil can, by recycling, be completely converted into gasoline. Temperatures in the range 850 to 950°F. (450 to 510°C.) and pressures of 3,000 lb. are required. The process involves high operating costs, expensive equipment, and an adequate supply of hydrogen. For these reasons it seems unlikely that the process will be an economical one for the production of gasoline in the near future. The attractive feature of the process is its ability to convert heavy oils completely to produce a volume of gasoline greater than the volume of charging stock (105 to 118 per cent yields by volume) without producing any heavy residuum or coke. It seems evident that in the presence of the catalyst, hydrogen combines with the cracked fragments which in a purely thermal process would polymerize to form the heavy residuum. Thus even the heaviest material is kept within the cracking-stock range and may be recycled until conversion to gasoline is complete.

[1] For an excellent flow sheet of a combination unit see "Elements of Petroleum Refining," p. 342.

Although the process is not very important today for the production of gasoline, it is used to a limited extent for improving the quality of inferior grades of lubricating oils and for the production of some high-octane aviation fuels by the hydrogenation of "polymer" gasoline. Furthermore, the process is almost certain to grow in importance as our reserves of crude oil decrease. The process is already widely used in many foreign countries for the production of motor fuels and oils from bituminous coal, lignite, coal tars, shale oils, and similar raw materials (Bergius process).

Catalytic Re-forming.—Straight-run gasolines rarely possess the octane ratings required in fuels for modern automobile engines (page 54). During the last few years, catalytic re-forming has become an important process for improving octane quality. The process is very similar to catalytic cracking; vapors of the low-octane stock are brought in contact with suitable catalysts at about 950°F. (510°C.) and 200 lb. pressure, resulting in the production of 77- to 80-octane gasoline with yields of 80 to 85 per cent. Catalysts have considerably longer life in re-forming than in catalytic cracking processes. In the process, *dehydrogenation*, leading to the formation of considerable hydrogen gas, and *aromatization* occur, and the increase in the amounts of unsaturated and isomeric chain hydrocarbons and of aromatic and other cyclic hydrocarbons in the gasoline accounts for its improved octane quality.

At the present time a closely related process for producing large quantities of the aromatic hydrocarbon toluene from petroleum hydrocarbons is receiving much attention because of the great demand for toluene in making the high explosive TNT (trinitrotoluene).

"Polymer" Gasoline.—The gasoline to which this name is applied is made from the hydrocarbon gases in natural gas or refinery gases. The processes for making polymer gasoline are the opposite of cracking inasmuch as large molecules are made from smaller ones. In general these processes may be divided into (1) thermal polymerization and (2) catalytic polymerization.

True catalytic polymerization can be applied only to hydrocarbon gases that are unsaturated, such as ethylene, propylene, and butylene. Limited amounts of these gases are produced in cracking operations, but they are almost entirely absent in field gases from oil and gas wells. The latter consist primarily of saturated paraffinic hydrocarbons. To make polymer gasoline by the catalytic method, the unsaturated hydrocarbon gases are passed over a

suitable catalyst at pressures of 500 to 1,400 psi and at temperatures of about 300°F. (150°C.) when the catalyst is new. As the catalyst gradually loses its activity, the temperature is raised. When a temperature as high as 500°F. is required to make polymerization occur at a satisfactory rate, the catalyst is replaced and the temperature dropped. When the catalyst is new, about 98 per cent of the unsaturated gases will be polymerized, but the conversion drops to 75 to 85 per cent just before the catalyst is discarded. A number of the successful catalysts consist of phosphoric acid deposited on fuller's earth or other suitable porous support. Thus far it has been uneconomical to reactivate the catalyst for re-use. Depending upon the catalyst and the impurities in the raw materials which may act as poisons (*e.g.*, hydrogen sulfide), 1 lb. of catalyst may serve to produce as little as 35 gal. or as much as 300 gal. of polymer gasoline. Catalytic polymerization units cost less per barrel of daily production than thermal polymerization units. However, the limited supply of unsaturated raw materials restricts their use.

Thermal polymerization has the advantage that it may be applied to the production of polymer gasoline from both saturated and unsaturated hydrocarbon gases. One thermal process employs temperatures from 900 to 1050°F. (480 to 566°C.) and pressures of 500 to 800 psi. Another successful one uses temperatures from 950 to 1100°F. (510 to 590°C.) and pressures of 1,200 to 1,600 psi. In these processes, saturated hydrocarbons are cracked and lose hydrogen, and the fragments polymerize and combine to form larger molecules. The unsaturated hydrocarbons also polymerize and there is evidence that some *alkylation* occurs.

Polymer gasoline made by the thermal process will have an octane number in the range 80 to 82; catalytic polymer usually is of 84- to 85-octane quality. It is an interesting and important fact that polymer gasolines are more effective in raising the octane number when blended with low quality gasolines than the above figures would indicate. In blending, they behave as though they possessed octane numbers in the range 90 to 120.

Catalytic Alkylation.—This is a new process for producing high-octane material that has engaged the attention of all the major oil companies because of the urgent demand for large quantities of high-octane airplane fuel. When a branched-chain saturated hydrocarbon and an unsaturated hydrocarbon are passed through a bath of concentrated sulfuric acid (catalyst) at low temperature

and low pressure, the two combine to form a larger molecule, which has a volatility in the gasoline range and possesses high antiknock value. For example, isobutane from uncracked field gases and butylene from cracked refinery gases may thus be combined to form isooctane. In practice the hydrocarbons combined are not pure substances and the product is a mixture of high-octane (90 to 95) alkylates with isooctane as the predominant product.

Various modifications of the above catalytic process have been devised and alkylation also has been accomplished by a thermal process using pressures of 4,000 to 5,000 psi at a temperature of about 950°F. (510°C.).

Gasoline Treating and Blending.—Gasolines produced by the various processes already described usually must be blended and subjected to some further treatment before they are sold as motor fuels.

Blending of various gasoline stocks is practiced to give a finished motor fuel that will perform properly at the atmospheric temperature and altitude conditions under which it will be used. Volatilities (boiling ranges) and octane ratings of the various stocks must be known to control scientifically the operating characteristics of the blended motor fuel (page 54).

Gasolines are treated for one or more of the following reasons: (1) to make them noncorrosive, (2) to improve their odor, (3) to improve or stabilize their color, and (4) to decrease the tendency to oxidation and gum formation. Until recently it was common practice to treat gasoline, especially cracked gasoline, with sulfuric acid to improve its stability and odor. Acid treatment was followed by water and alkaline washes to neutralize remaining acid and sometimes by redistillation. This practice has now been largely abandoned unless the stocks contain excessive amounts of sulfur. Most refiners now make their gasolines sufficiently stable with respect to color, oxidation, and gum-forming tendency by use of the Gray process or by the addition of small concentrations of various "oxidation inhibitors,"[1] or by a combination of the two methods. In the Gray process, gasoline vapor from the top of the bubble tower passes downward through upright cylindrical vessels filled with fuller's earth (an aluminum silicate clay). In contact with the fuller's earth, there is a selective catalytic polymerization of certain highly active unstable compounds formed during cracking, those

[1] LOWRY, *Trans. Electrochem. Soc.*, **69**, 185 (1936). ELLEY, *ibid.*, **69**, 195 (1936).

compounds which unless removed lead to the formation of substances of undesirable color, and of gums. Sulfur compounds are undesirable in gasoline from the standpoint of odor. Also, they adversely affect the octane rating and decrease the response of a gasoline to the addition of tetraethyl lead. Fortunately, in the catalytic processes of cracking and re-forming, much of the sulfur is converted to hydrogen sulfide which is easily removed. If necessary, sulfur may be removed or converted into harmless compounds by a "sweetening" process that involves agitating the gasoline with a solution of lead oxide in caustic soda.

LUBRICANTS

When one solid surface is moved relative to another solid surface with which it is in contact, there is a frictional resistance to motion. If the surfaces are perfectly smooth, the frictional resistance arises primarily from the operation of molecular forces of cohesion. With practical surfaces, which are not perfectly smooth, the interference of minute projections on the surfaces contributes to the resistance. This frictional resistance causes surface wear and the dissipation of energy as heat. To hold energy dissipation and surface wear to a minimum in all sorts of machines, a lubricant is used to keep the moving surfaces apart. Most lubricants are oils or greases. However, in special circumstances other fluids (water, air, etc.) and solids (graphite) may perform this important function.

Before the rise of the petroleum industry, lubricating oils were "fatty" oils of animal or vegetable origin such as castor oil, rapeseed or colza oil, lard oil, tallow oil, neat's-foot oil, and sperm oil. Although these oils still are used to a limited extent, especially as additions to petroleum oils and as raw materials for the manufacture of greases, they have been replaced by lubricating oils from petroleum for most purposes. Fatty oils suffer the handicaps of relative high cost, a tendency to hydrolyze in contact with moist air and aqueous mediums, and a greater tendency to oxidize and thicken in contact with air than is possessed by petroleum oils.

Principles of Lubrication.—In all cases, a lubricant should adhere to the moving solid parts so that there is a shearing of the lubricating layer. A good lubricant is, then, one that adheres well to the surfaces and offers but little resistance to shearing, or, in other words, that has but little friction between its own moving particles. The term *viscosity* is used in designating the amount of this internal friction. An oil that flows sluggishly is said to possess a high

viscosity. A lubricating oil should have sufficient adhesion and viscosity to enable it to stay in place, but if it possess greater viscosity than necessary, power will be wasted in shearing the oil. In selecting lubricants, it is a good principle to use the thinnest (least viscous) oil that will stay in place and do the work. With a well-balanced shaft or journal running at moderately high speed and under fairly light pressure there may be perfect fluid-film lubrication. Under these circumstances, a liquid film keeps the moving surfaces well apart and the viscosity of the lubricant is its most important characteristic since the frictional resistance is due solely to the shearing of the liquid. On the other hand, with very low speeds or high pressures, or both, or when starting after a period of rest, the lubricant tends to be squeezed out of the bearings with a resulting increase in the friction coefficient. At sufficiently high pressure, direct metal-to-metal contacts may be established. In such circumstances, a property of lubricants known as "oiliness" may be far more important than their viscosity. Oiliness is usually defined as that property of a lubricant by virtue of which one lubricant gives a lower coefficient of friction at low speeds or high loads than another fluid of the same viscosity. This property undoubtedly is related to the tenacity with which a given oil adheres to a metal surface to form a film of thickness at least equivalent to several molecular diameters.

It has long been known that fatty oils possess an oiliness superior to plain lubricating oils from petroleum. The latter, however, may be greatly improved in this characteristic by small additions of high-molecular-weight polar organic compounds such as oleic acid. Such additions are made in the production of "high-pressure" lubricants, which are used, for example, in the lubrication of automobile gears where pressures between the gear teeth may reach values as high as 400,000 psi with rubbing velocities up to 300 ft. per min.

Lubricating Oil Fractions from Crude Oil.—For use in automobiles, airplanes, and for other industrial purposes, it is necessary, in this country, to supply about 1 gal. of lubricating oil for every 25 gal. of gasoline consumed. This large demand for lubricating oil has made it necessary to produce lubricants of good quality from crude oils that formerly were considered unsuitable for the purpose. As a consequence, processes and equipment that were unheard of a decade ago are now available for separating and refining lubricating oil fractions.

All lubricating oil fractions are contained in the heavier portion of the crude that remains after distilling off gasoline, kerosene, and low-viscosity gas oils, *i.e.*, in the residuum from the "skimming" or "topping" operation (page 84). For the production of lubricating oils, the residuum is first subjected to a vacuum distillation. Lower pressures, usually below 40 mm. absolute, permit distillation at comparatively low temperature with the result that there is less thermal decomposition (cracking) of the oil. Thus, lubricating oils of better color, higher viscosity, better stability, and greater resistance to oxidation may be produced than would be possible if distillation was accomplished at atmospheric pressure.

The residuum to be vacuum distilled is passed through a pipe still where it is carefully heated to such a temperature that all the fractions to be recovered as distillates will vaporize as the stream enters the evaporator section of a bubble tower. In most cases, considerable quantities of steam are introduced into the system to accomplish vaporization of the desired components at lower temperatures than would otherwise be possible (steam distillation).[1] A similar effect may be obtained by introducing low-boiling gas oils. Because of the large vapor volume, bubble towers for vacuum distillation units must be considerably larger than bubble towers for cracking units or skimming units.

In the usual practice, the bubble tower separates the vapors into two or possibly three fractions. A heavy residuum, leaving the bottom of the tower, may be finished as asphalt or road oil or may be used directly as heavy fuel oil. The lightest overhead fraction is known as wax distillate; it contains the crystalline paraffin waxes, the lighter type of lubricating oil known as neutral oil or pale oil, various undesirable constituents in small amounts, and any gas oil intentionally introduced as an aid in distillation and in subsequent dewaxing. The heavier cut contains wax of a different type generally known as amorphous wax, high-viscosity lubricating oil of the "cylinder stock" or "bright stock" type, and varying amounts of asphaltic and other undesirable constituents. If the crude oil is one that contains only small amounts of asphaltic substances, wax distillate alone may be removed as an overhead product and the entire residuum treated, without distillation, for the production of cylinder stock. Pennsylvania crudes are outstanding examples

[1] See GETMAN and DANIELS, "Outline of Theoretical Chemistry," 6th ed., John Wiley & Sons, Inc., New York (1937), or any standard textbook of physical chemistry.

of this type, but cylinder stock may be made from some other crudes by this method of processing. However, for most mixed-base and asphaltic-naphthenic-base crudes, the cylinder stock fraction is obtained as an overhead product as outlined above. In some refineries, another overhead cut, intermediate to the two just mentioned, is taken. It will contain a lubricating oil fraction with a viscosity between that of neutral oil and cylinder stock, and will contain some wax of each type; the term "slop wax" is sometimes applied to this mixture of crystalline and amorphous waxes.

Dewaxing Lubricating Oil Fractions.—To produce lubricating oils from the above fractions, which will properly function as lubricants and hence will not congeal at subnormal temperatures, *i.e.*, to produce oils of sufficiently low "pour point" (page 102), it is necessary to remove a major portion of the dissolved waxes. Until comparatively recently, separate methods were employed for removing wax from the two lubricating oil fractions. In the last few years new, more general methods of solvent dewaxing have been developed and are growing in importance. Nevertheless, the older methods are still widely used and deserve brief mention.

The orthodox method for separating crystalline wax from the lighter lubricating oil fraction (wax distillate) consisted of a slow chilling of the fraction as such, or after suitable dilution with naphtha, by artificial refrigeration. The well-defined wax crystals were then separated by a filter pressing operation, yielding a cake of crude scale wax and a filtrate which by further reduction by distillation and treatment became "neutral" or "pale" lubricating oil stock. The crude scale wax contains 30 to 40 per cent of oil which is removed by "sweating," the wax being placed in shallow pans with false bottoms and the temperature gradually increased. After sweating and filtration of the molten wax by percolation through fuller's earth, the ordinary refined paraffin wax of commerce is obtained.

The removal of the amorphous wax (petrolatum) from cylinder stock fractions is accomplished by diluting with about twice the volume of naphtha and chilling the solution to a temperature 20 to 40°F. below the pour point desired in the finished oil. The precipitated amorphous wax is separated from the oil-naphtha solution by passing the mixture through high-speed centrifuges (17,000 r.p.m.). A small percentage of the petrolatum is refined and finds various pharmaceutical and industrial uses, but the major portion is blended with other cracking-unit charging stocks. The oil-naphtha solution from the centrifuges is converted into refined cylinder or bright

stock for lubricants by treatment, percolation, filtration, and removal of the naphtha by vaporization.

The recent general method[1] for dewaxing lubricating oil fractions consists of mixing the wax-bearing oil with the proper volume of suitable solvent, refrigerating the mixture to the required temperature to bring about a precipitation of the wax, and then separating the wax from the oil by charging the mixture on continuous filters or putting it through centrifuges. After the dewaxing operation, the solvent is separated from the oil by distillation and the wax-free oil is ready for further refining. Small amounts of solvents retained by the wax also are removed by distillation. Studies on the dewaxing process have been made with a great variety of solvents and solvent mixtures, and it seems certain that this research will lead to useful commercial processes. At the present time, the principal dewaxing solvents used in the United States, in order of relative importance, are (1) a mixture of benzene and acetone, (2) propane, (3) a mixture of benzene and ethylene dichloride (Bari-Sol process), and (4) trichloroethylene (Separator-Nobel process).

Propane as a precipitative solvent offers interesting possibilities, which already have been applied to a certain extent in practice. If the oil is mixed with about 3 or 4 volumes of propane under a pressure of 200 psi or higher to prevent evaporation losses and the solution is brought to a temperature of around 120°F. (50°C.), the asphaltic material in the oil will be largely precipitated. After separation of the asphaltic precipitate, the volume of propane is reduced and the remaining solution is simultaneously cooled to −40 to −45°F. by evaporation of a proper proportion of the propane. The wax separates from the concentrated, refrigerated solution and is removed from the oil by the methods already described.

Acid Refining of Lubricating Oils.—Most dewaxed lubricating oil fractions still contain naphthenic, asphaltic, and other undesirable constituents, which must be largely removed to produce a finished lubricating oil. Although 60 to 70 per cent of the oils produced in the United States are now finish-refined by solvent-treating processes, the older acid-treating process still retains considerable importance; indeed, it is used with modifications as an adjunct to many solvent-treating processes.

In the acid-treatment process, oil is thoroughly agitated with the required amount of concentrated sulfuric acid, which acts purely as

[1] Kalichevsky, "Modern Methods of Refining Lubricating Oils," pp. 43–79 Reinhold Publishing Corporation, New York (1938).

a solvent for some of the constituents and reacts chemically with others to form a tarry sludge. The sludge may be used directly as a fuel or it may first be treated with hot water to recover acid. The oil, after acid treatment, is neutralized with caustic soda or ammonia, or by being brought in contact with finely divided fuller's earth at temperatures in the range from 225 to 450°F. (108 to 230°C.). The latter treatment also serves to decolorize and stabilize the oil. With many stocks the final refining step is a percolation filtration through fuller's earth.

Solvent Refining of Lubricating Oils.[1]—The general scheme of solvent refining methods is to bring the oil into intimate contact with a solvent that is immiscible with the oil in a continuous countercurrent operation. A suitable solvent will be one in which the undesirable naphthenic, asphaltic, and resinous constituents are more soluble than they are in the oil. The process produces, then, a refined oil consisting principally of paraffinic hydrocarbons, but containing some solvent that may be recovered by distillation leaving the refined lubricating-oil stock. The solvent with the various constituents extracted from the oil is the other product of the process. The solvent is recovered by distillation and recycled. The extracted residuum is of more value than the sludge from the acid-treatment process because it can be used as cracking-stock blending material, as a satisfactory fuel, or as a source of asphalt. In solvent treating, the action is entirely that of physical extraction, no chemical reaction being involved.

Much research and development work on solvent refining are in progress and one may expect the use of new solvents and new conditions to produce lubricating oils of more desirable characteristics. The principal single solvents in use today, roughly in order of importance, are furfural, phenol, *pp'*-dichloro-diethyl ether ("chlorex"), and nitrobenzene. Mixtures of sulfur dioxide and benzene also are used, and one important process (Duo-Sol) uses two solvents: propane, which dissolves the desired paraffinic fraction and decreases the solubility of undesirable constituents in this fraction, and a mixture of phenol and cresol, which is immiscible with the oil-propane solution and is a good solvent for the naphthenic, asphaltic, and resinous constituents.

Applied to the same medium-grade raw lubricating-oil fractions, the solvent-treating methods are somewhat more economical than acid treatment. Solvent treatment affords somewhat higher yields

[1] KALICHEVSKY, *op. cit.*, pp. 80–167.

of finished oil, and the product usually is characterized by having a lower *carbon residue* (page 101) and a higher *viscosity index* (page 100) than oils produced by the older process. On the other hand, solvent-refined oils seem inferior in oxidation resistance, oiliness, tendency to thicken in use, and tendency to form films of lacquerlike deposits on the heated working parts of engines which cause sticking of piston rings. Since the oxidation products of oils are generally acidic in nature, solvent-refined oils may develop corrosive tendencies during use. It appears certain that the raw lubricating-oil fractions contain natural inhibitors to oxidation, which are almost completely removed by solvent treatment but are not completely removed by acid treatment. One great advantage of the solvent-treating method is that it makes possible the production of suitable lubricating oils at reasonable cost from crude oils that could not be considered a possible source of lubricants when only the older acid-treating method was available.

A recognition of the defects of solvent-treated oils led to a successful search for substances that could be added in small amounts to these oils to improve their resistance to oxidation, to restore and even greatly improve oiliness, and to decrease the tendency to thicken in use. Before these addition agents for the improvement of oil character are discussed, the properties important in characterizing a refined oil should be given some attention.

Properties of Refined Oils.[1]—The most important properties of lubricating oils that determine their performance in service or are used in specifications are gravity, viscosity, viscosity index, carbon residue or coke number, color, oxidation stability, cloud point, pour point, flash point, and fire point.

In the petroleum industry, gravities are usually expressed in A.P.I. degrees, although specific gravity, densities in various units, and gravities on the two Baumé scales may be used. The relations between gravities in these various systems have already been discussed (page 52).

As has been indicated, the *viscosity* of a lubricating oil is one of its most important properties because it is a measure of the internal friction in the fluid. In absolute units, "poises,"[2] the viscosity

[1] A.S.T.M. Standards on Petroleum Products (1939), Am. Soc. Testing Materials, Philadelphia. KALICHEVSKY, *op. cit.*, pp. 11–21.

[2] There is a corresponding English or engineering unit of absolute viscosity, which has the dimensions of pounds per square feet per second. 1 engineering or English viscosity unit = 14.88 poises.

represents the force in dynes that is necessary to give 1 sq. cm. layer of fluid a velocity of 1 cm. per sec. relative to another parallel layer 1 cm. away. The "centipoise" equal to 0.01 poise is frequently employed as a unit of viscosity. The viscosity of water at 20°C. (68°F.) is 1 centipoise, hence viscosities on any scale relative to water at 20°C. (relative viscosities) also are absolute viscosities in centipoises. In the petroleum industry in the United States, viscosities are almost invariably expressed on an arbitrary scale as the number of seconds required for 60 cc. of the oil to run through a standard orifice from a cylinder filled to a definite level at a standard temperature. The instrument used for making these measurements is the Saybolt Universal Viscosimeter,[1] and the viscosities thus determined are called Saybolt Universal viscosities (S.U.V.). Saybolt viscosities of an oil usually are determined at one or more of the following temperatures: 100, 130, and 210°F. Empirical equations have been devised for calculating absolute viscosities[2] from Saybolt viscosities and from viscosities on other arbitrary scales in practical use.

The Society of Automotive Engineers has assigned numbers (S.A.E. numbers) to lubricating oils whose Saybolt viscosities lie within a certain range as indicated in Table 17.

TABLE 17.—S.A.E. NUMBERS AND SAYBOLT VISCOSITIES OF OILS

S.A.E. number	S.U.V. range, sec.			
	At 130°F.		At 210°F.	
	Min.	Max.	Min.	Max.
10	90	Less than 120		
20	120	Less than 185		
30	185	Less than 255		
40	255	....	...	Less than 75
50	...	....	75	Less than 105
60	...	....	105	Less than 125
70	...	....	125	Less than 150

The kinematic viscosity, which is the absolute viscosity divided by the density (grams per cubic centimeter, or pounds per cubic foot), is not used in writing specifications for lubricating oils, but

[1] A.S.T.M. Standards (1939), Part III, p. 216.
[2] See, GARNER and KELLY, *Physics*, **4**, 97, (1933).

it has some significance in the theory of lubrication and in problems on the flow of fluids.

In many types of service a lubricating oil must function in a machine over a considerable range in operating temperature. When this is due to normal seasonal variations in atmospheric temperatures, adjustments may be made by selecting an oil of suitable viscosity for each season. A much more difficult situation is encountered in oils for automobile, airplane, and other internal-combustion engines where the lubricant must function at the low starting, as well as at the much higher normal operating temperatures. An oil which had the same viscosity over this entire temperature range would be ideal but impossible, because all lubricants decrease in viscosity as the temperature is increased. However, it has long been known that oils from different types of crude petroleum possessed considerably different viscosity-temperature coefficients. With oils made by the older refining methods, those from Pennsylvania-type crudes thinned down the least and those from Gulf Coast crudes the most as the temperature was increased. This was one of the properties that contributed "premium quality" to lubricating oils made from Pennsylvania crudes.

The present-day method of expressing the rate at which the viscosity of an oil will change with temperature is by stating its *viscosity index*, the higher the viscosity index, the lower the rate at which its viscosity decreases with increase in temperature. If the S.U.V. of an unknown oil is determined at 210°F. and at 100°F., its viscosity index may be calculated by comparison with the viscosities at 100°F. of two standard oils that have the same viscosities as the unknown at 210°F. One of these reference oils will be from a standard set made from Pennsylvania crude and assigned viscosity indexes of 100; the other will be from a standard set to which viscosity indexes of 0 have been assigned.

$$\text{Viscosity index of } X = \frac{V_L - V_X}{V_L - V_H} \times 100$$

where V_L = S.U.V. at 100°F. of the low-viscosity-index standard oil which has the same S.U.V. at 210°F. as X.

V_X = S.U.V. at 100°F. of the unknown oil, X.

V_H = S.U.V. at 100°F. of the high-viscosity-index standard oil which has the same S.U.V. at 210°F. as X.

For example, an oil of unknown viscosity index has an S.U.V. of 60 sec. at 210°F. and of 600 sec. at 100°F. The 100-viscosity-

index standard oil[1] which has an S.U.V. of 60 sec. at 210°F. will have an S.U.V. at 100°F. (V_H) of 426 sec. The low-viscosity-index standard oil which has an S.U.V. of 60 sec. at 210°F. will have an S.U.V. at 100°F. (V_L) of 781 sec.

$$\text{Viscosity index of } X = \frac{781 - 600}{781 - 426} \times 100 = 51$$

Solvent refining usually produces an oil of slightly higher viscosity index than could be produced from the same raw lubricating-oil fraction by the acid treatment.

Although a high viscosity index is desirable in motor oils and much effort is expended in improving the viscosity index of oils by refining, it should be emphasized that viscosity-temperature characteristics are of little or no importance for oils that are to function at approximately constant temperature, such as turbine oils.

The *carbon residue*, or *Conradson carbon*, test on oils is made by vaporizing a weighed sample of oil in a standard apparatus by a standard procedure;[2] the residue is weighed and expressed as percentage of the charge. The carbon residue was supposed to be a measure of the carbonizing properties of a lubricating oil and hence of the amount of deposit that might be expected in engines. The present opinion seems to be that the carbon residue tests can be correlated to the tendency to form engine deposits only when the oils are made by similar methods from similar stocks.[3] There is a better correlation between engine deposits and the *carbonization index* of an oil, which is defined as the temperature at which 90 per cent of the oil has distilled over under a pressure of 1 mm. Hg.

It is generally agreed that *color*, as well as *fluorescence*, has little relation to oil quality. However, owing to the buying habits of the public, color still is written into specifications and hence is important in the industry. Consumers have for so long associated the characteristic "bloom" or fluorescence of Pennsylvania oils with high quality that many refiners find it necessary to add "fluorescence improvers" to their product even though they contribute nothing to oil quality. The color of an oil is expressed on various arbitrary scales and is determined by making comparisons with standards in

[1] See, A.S.T.M. Tentative Standard D341-32T. NEWELL, *Ind. Eng. Chem.* **23**, 843 (1931). KALICHEVSKY, *op. cit.*, pp. 11–14, 205.

[2] A.S.T.M. Standard D189-39.

[3] GRUSE and LIVINGSTONE, pp. 1–20, A.S.T.M. Symposium on Lubricants (March, 1937).

standard instruments called colorimeters. In the United States the most frequently used instruments are the Union Colorimeter,[1] Tag-Robinson Colorimeter, the Lovibond Tintometer, and the Saybolt Chromometer.[1]

In applications in which an oil is used for a long period of time such as in automobile engines, its *oxidation stability* is an important characteristic because this property seems related to sludge formation, carbonization, thickening, and the development of oil acidity during service. The most reliable tests for oxidation stability are actual engine and service tests. Because these tests are expensive and time consuming, a variety of short-time standard tests at higher temperatures and sometimes with catalysts have been devised.[2] Many of these tests are of value if the results are interpreted with caution.

For lubricants that must function at low temperatures (motor oils, etc.), the *pour point* is important. The pour point is the temperature at which the oil ceases to flow when cooled at a standard rate in a standard container.[3] In general, the more completely the wax has been removed in refining, the lower will be the pour point of the oil. Recently it has been discovered that certain substances, called "pour-point depressants," may be added to oils to lower their pour points. The *cloud point* is the temperature, in a standardized test, at which cloudiness develops due to the separation of wax. The cloud point occurs at a higher temperature, of course, than the pour point.

When oils are heated in a standard vessel at a standard rate, the temperature at which the vapors will ignite by flashing, but will not continue to burn, when an open flame is passed over the oil, is called the *flash point*,[4] and the temperature at which the oil will burn continuously is called the fire point.[4] Flash and fire points are of obvious practical importance for transformer oils and other special use oils. For motor oils, their principal significance is as an indication of volatility, and to detect the presence of small amounts of substances, such as solvents, which are much more volatile than the bulk of the oil. Some correlation has been shown between these properties and oil consumption in engines.[5] Other standard tests,

[1] A.S.T.M. Tentative Standards D155-39T, D218-25T.

[2] Kalichevsky, *op. cit.*, pp. 18, 209.

[3] A.S.T.M. Standard D97-39.

[4] A.S.T.M. Standard D92-33.

[5] Davis and Best, *Nat. Petroleum News*, **27**, 70 (1935). Danse, *ibid.*, **27**, 38 (1935).

such as those for determining the "neutralization number," "saponification number," and "precipitation number" of oils, and the "steam emulsion test" are of some value in following the changes that take place in oils during service or in determining the suitability of an oil for a specific application.

Addition Agents for Motor Oils.[1]—The prime object of the refining methods that have been described has been to improve the characteristics of lubricating oils by the removal of undesirable constituents. In recent years, much progress has been made in the further improvement of refined oils by the addition of relatively small amounts of various substances. Although some addition agents serve to improve more than one characteristic of an oil, they may in general be classified as follows:

1. *Pour-point Depressants.*—These, added in small amounts, lower the pour point. With these additions, it is not necessary to remove wax so completely and the viscosity index is thereby somewhat improved. Two of the most effective patented commercial depressants are Paraflow[2] and Santopour.[2] The addition of 1 per cent of the former to an S.A.E. 10 motor oil lowered the pour point from +30 to −10°F., and it is reported that 0.16 per cent of the latter lowered the pour point of an S.A.E. 30 oil from +20 to −15°F.

2. *Viscosity Index Improvers.*—These, in general, are stable high-molecular-weight compounds that disperse colloidally in the lubricating oil. Exanol is the trade name for one such product which is a heavy resinlike material obtained by polymerizing unsaturated hydrocarbons. These substances are most effective when added to low-viscosity-index oils. Thus, the addition of 0.5 per cent of Exanol is reported to raise an oil of V.I. = 26 to V.I. = 51; an oil of V.I. = 91 to V.I. = 100; and a Pennsylvania oil of V.I. = 100 to V.I. = 106.

3. *Oiliness Carriers.*—The importance of the quality called "oiliness" in lubricants for high-pressure service has already been mentioned. It also has been mentioned that fatty oils are superior to petroleum oils in this characteristic. The principal addition

[1] MAVERICK and SLOANE, "Symposium on Lubricants," pp. 53–66, A.S.T.M. March, 1937. KALICHEVSKY, *op. cit.*, pp. 168–199. REIFF, *Ind. Eng. Chem.*, **33**, 351 (1941).

[2] Paraflow is a condensation product of chlorinated wax and naphthalene formed in the presence of aluminum chloride as a catalyst. Santopour is obtained by condensing phenol with chlorinated wax in the presence of aluminum chloride, followed by a further condensation with phthalyl chloride.

agents of this class are the high-molecular-weight fatty acids, such as oleic, stearic, and cerotic, and the chlorinated esters of these same fatty acids.

4. *Oxidation Inhibitors.*[1]—Stability in service is one of the most important characteristics of oils for internal-combustion engines, transformers, turbines, and a number of other uses. It is believed that raw unrefined lubricating-oil fractions contain some natural inhibitor substances, which are largely removed in refining operations with the result that a finished oil is less resistant to oxidation than the stock from which it was made. It has been found possible greatly to improve the resistance of finished oils to oxidation by the addition of a few tenths or even a few thousands of a per cent of various inhibitor substances. Aromatic phenolic compounds, aromatic amines, sulfur compounds, organometallic compounds, and various organic compounds containing chlorine are among the substances that are effective as oxidation inhibitors.

5. *Corrosion Inhibitors.*—It also has been found possible to add substances (page 427) to an oil that will inhibit the attack on metal even though corrosive substances are formed by oil oxidation. These substances are usually organic compounds containing phosphorus (Santolube C.C.), arsenic, antimony, bismuth, chromium, tin, or lead.

6. *Fluorescence and Color Improvers.*—These have no effect on the important characteristics of a lubricating oil. Since they are used, if they are used, solely to make an oil more acceptable to consumers, no further space will be devoted to them here.

The whole subject of the improvement of oil quality by the use of addition agents is in a state of rapid development and the future will undoubtedly bring new oils that are "tailor-made" for specific applications.

Lubricating Greases.—A commonly accepted definition[2] of a lubricating grease is that it is "a semisolid or solid combination of a petroleum product and a soap or a mixture of soaps, with or without fillers, suitable for certain types of lubrication." For heavy pressures and slow speeds, greases may be employed as lubricants, but it is not under these conditions alone that greases are used. They may be employed for other reasons; *e.g.*, to prevent oil from being thrown from the bearings, as in textile mills, and when it is desirable to lessen the attention that bearings require. In general,

[1] Davis, Lincoln Byrkit, and Jones, *Ind. Eng. Chem.* **33**, 339 (1941).
[2] A.S.T.M. Standards on Petroleum Products and Lubricants (1939).

however, because of the greater amount of work that must be done in shearing the lubricating film, greases show higher coefficients of friction than oils. An oil, instead of a grease, should be used whenever possible.

Cup greases are essentially emulsions of petroleum lubricating oils with water, stabilized with calcium soaps of such fatty acids as oleic and stearic acids. These calcium soaps will dissolve in heated petroleum oils and on cooling will form a gel. If the mixture is anhydrous, the gel will be unstable and globules of oil will tend to separate. If an excess of lime is present, the gel will be particularily unstable; when stirred, the soap will precipitate and the gel structure will be destroyed. If water is added at a temperature of about 190°F. (90°C.), a stable product may be formed. The amount of emulsified water in a grease is usually less than 1 or 2 per cent. Calcium soaps yield emulsions of the water in oil type.

A typical procedure for making grease may be described as follows: Molten tallow is pumped into a cast-iron steam-jacketed kettle equipped with slowly rotating scraping agitators. High-grade hydrated lime is added in sufficient amount to form the calcium soaps of the fatty acids in the tallow; the glycerin formed in the saponification is not removed. When the soap has been formed, warm petroleum oil of proper grade is added and the whole mass well mixed. At the temperatures involved, the mixture is quite fluid and is drawn from the bottom of the kettle into suitable containers. Typical greases contain 10 to 25 per cent of calcium soap and lubricating oil stocks with S.U.V.'s in the range from 100 to 200 sec. at 100°F. (37.8°C.). If the grease is to be used in grease "guns" for servicing automobiles, the oil employed may have an S.U.V. of 300 sec. or more at 100°F. These heavier greases offer more resistance to being forced out of a bearing.

Soda-base greases contain sodium soaps of fatty acids and a petroleum lubricating oil. These greases are practically anhydrous, but if water is present, an emulsion of the oil in water type will form. If the grease is produced by saponifying the fatty substance in the presence of the lubricating oil, a heavy sponge of fibrous structure is produced. Because of their appearance, these greases frequently are called *fiber greases*. Sodium soaps are soluble in water, hence these greases would not be suitable for service in contact with water. Nonfibrous soda-base greases containing heavy black asphalt-base petroleum residues are widely used for lubricating automobile transmission and differential gears.

Lead-soap greases also are employed to a considerable extent for lubricating automobile transmissions. The addition of sulfur above that carried by the oil is reported to increase the "oiliness" of the product. For special applications, greases containing soaps of still other metals such as aluminum are used.

Rosin-oil grease (*set grease, axle grease*) is made from slaked lime and rosin oil, with or without the addition of petroleum oil. The lime may be incorporated by sifting dry slaked lime into the rosin oil with constant stirring, or by adding a lime cream previously prepared from either water and slaked lime, or a light grade of petroleum oil and slaked lime. In the latter case, a little rosin oil is first added to the petroleum oil so that a small amount of rosin soap will be formed before the lime is added to the bulk of the rosin oil. After the lime and rosin oil have been thoroughly mixed, they are allowed to stand and the mass quickly sets to a stiff grease, frequently in less than 5 min. If any water is present, it is expelled from the grease during setting and is then withdrawn. The grease may be thinned if desired by incorporating a petroleum lubricating oil. The setting of the grease is caused by the saponification of the rosin oil.

These set greases are employed as axle greases. For this purpose, mica, talc, and similar mineral substances are frequently added as fillers to increase the resistance of the grease to being squeezed out under heavy loads. Rosin greases may be used on any heavy slow-moving bearing, being frequently used as gear greases and to lubricate the curves in street-railway tracks.

For standard methods of analysis for greases including tests for consistency, water, neutralization number, dropping point, stability, etc., the reader is referred[1] to standard treatises.

Graphite as a Lubricant.—Graphite is the most widely used of all solid lubricants. It may be incorporated with metal (powder metallurgy) for bearings and, especially when service is intermittent, no other lubricant is necessary. It is said to serve well as a lubricant for cast-iron bearings where it acts as a surface evener of the porous metal. On finer surfaces it does not work so well, having a tendency to collect in such quantities as seriously to score or abrade the journal and bearing. To serve better as a lubricant, Acheson

[1] A.S.T.M. Standards on Petroleum Products and Lubricants (1939). Chittick, Evaluation of Petroleum Products, A.S.T.M. (1940), pp. 11–18. Many references to standard tests and to research on lubricating greases are given in the latter reference.

prepared artificial graphite in an extremely finely divided condition which is known as deflocculated graphite. High-purity artificial graphite is masticated with a solution of tannin, which serves as a protective colloid and disperses the graphite. After standing to permit settling of suspended matter the colloidal graphite dispersion is filtered under pressure through canvas impregnated with thin films of rubber, by which process a large part of the water is separated and a graphite paste, called *colloidal-graphited water*, is formed. By grinding the aqueous paste with oil, water can be displaced and a paste in oil obtained. The latter bears the commercial name *colloidal-graphited oil*. Deflocculated graphite has value as a lubricant but must be used with some caution. For example, it should not be used in the presence of electrolytes because they cause a coagulation of the graphite colloid, which may lodge in ball races and oil fuel lines and eventually interfere with oil circulation. *Oildag* is the name given to dispersions of the oil-graphite paste in lubricating oils. These usually carry about 0.35 per cent of colloidal graphite. *Aquadag* is a dispersion of the water-graphite paste in water and is said to be useful in place of the usual oil-and-soap mixtures for lathe and die threading, drilling, reaming, planing, and general machine-shop work. The latter is also said to be useful for air-compressor lubrication.

Graphite also finds use as a constituent of some lubricating greases, in which it may be present from small amounts up to as high as 25 per cent.

Cooling Liquids and Lubricants for Cutting Tools.—In the various machining operations, such as turning, planing, sawing, boring, threading, and milling, the tool employed becomes heated, especially at the cutting edge. To prevent overheating and injury to the tool, cooling or lubrication, or both, are provided. Water is an excellent cooling medium because it has a high specific heat and a high heat of vaporization; it has poor lubricating value, however. Its corrosive action on the tools, the machines, and the work is objectionable and may be considerably checked by the addition of soaps or other inhibitive alkaline substances. Nevertheless, the use of water is limited to rather simple operations such as rough turning and grinding.

Cutting fluids are available, which are drawn between the chip and the face of the tool and by their lubricating effect lessen the friction. Less heat is therefore dissipated and the tool is kept at a lower temperature. It has been learned by experience that straight

petroleum oils are very poor cutting lubricants; fatty oils are much superior, the situation being very similar to that encountered in extreme pressure lubrication. Lard oil and sperm oil are the most important cutting oils, although many other animal and vegetable oils are employed to a certain extent. Furthermore, turpentine, pine oil, and rosin oil find some use, as well as some compounded oils that are mixtures of fatty oils and petroleum oils.

If cooling as well as lubrication is desired, these properties may be found combined in the cutting emulsions that will contain about one part of so-called "soluble" oil emulsified with about four parts of water. Some "soluble" oils are mixtures of petroleum oil with a neutralized sulfonated oil, others are mixtures of petroleum oils with alcoholic soap solutions. The neutralized sulfonated oils and the soaps act as protective emulsoids to stabilize the oil-water emulsion.

Conditions under which lubrication must be provided are so varied and so many lubricants are available, that the engineer responsible for the operation and maintenance of modern equipment must possess considerable knowledge on this subject. In the absence of such knowledge, he had best rely upon the advice of the lubrication specialists in the employ of established, reliable producers of lubricants.

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CHAPTER III

REFRACTORIES

By J. C. WARNER, Ph.D.

The term *refractory* is applied to any material that has a high resistance to fusion and is suitable for use as linings for furnaces, converters, ladles, hot-metal storage mixers, furnace runners, and other equipment that must withstand high temperatures in the presence of gases, metals, slags, etc. Although the primary function of refractories is to withstand high temperatures, they usually are called upon to resist one or more of the following destructive influences: abrasion by dust-bearing gases, rapid changes in temperature, pressure, corrosion by slags and fluxes, or erosion by molten metals. Various combinations of the following physical properties of refractories are important in determining their utility: softening and fusion temperature, density, porosity, crushing strength, thermal conductivity, electrical conductivity, dielectric properties, specific heat, and coefficient of thermal expansion. As in all applications of engineering materials, the initial and upkeep costs are of prime importance in the selection of refractories for a given purpose.

The most widely used refractory materials are mortars, ramming mixtures, bricks, and other fired shapes made of fire clay, high alumina minerals and mixtures, silica, magnesite, chrome ore, and fosterite, $2MgO \cdot SiO_2$.

Fire Clay and Fire-clay Bricks.—Fire clays are hydrated aluminum silicates for which $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ may be considered the type formula corresponding to 39.5 per cent of alumina, 46.5 per cent of silica, and 14 per cent of water. The mineral kaolinite has almost exactly this composition but most fire clays contain at least small amounts of iron, calcium, magnesium, titanium, sodium, and potassium. At high temperatures the water is driven off from these hydrated silicates leaving a material consisting principally of alumina and silica. Fire clays may be divided into two classes: flint, or hard clays, and plastic, or soft clays. Intermediate between these are the semiflint and the semiplastic clays.

Deposits of flint clay are found in Pennsylvania, Maryland, Kentucky, Ohio, and Missouri. These clays are hard and dense and, after having been ground and mixed with water, their drying shrinkages and plasticity are very low. The shrinkage on firing is very high, but the best clays of this type are very refractory, having a *pyrometric cone equivalent* (P.C.E., see page 115) of cone 33 to 35. By proper silication and blending of semiplastic and plastic clays, products of a variety of degrees of refractoriness, plasticity, and bonding strength may be produced. The P.C.E. values of clays of this type range all the way from cone 26, for the clays of high plasticity, to cone 33.

Fire-clay brick is made from selected raw and calcined fire clays, the relative proportions of flint, plastic, and calcined clays depending upon the properties desired in the brick. The most refractory brick consists largely of flint clay. At least four or five grades of fire-clay brick are produced. In recent years a high-grade fire-clay brick has been made by the "power-press" method that produces a very dense, highly refractory brick which has unusually good resistance to slag attack and thermal spalling, and good strength at high temperatures. The ranges of composition and some of the properties of the several grades of firebrick are given in Table 18.

High Alumina Refractories.—In this class are found those materials which contain 50 per cent or more of alumina. They are made in general from high alumina minerals such as bauxite, corundum, and diaspore clay, or from mixtures of these high alumina minerals with fire clay. Most high alumina refractories are made from diaspore clay, either alone or blended with flint or plastic fire clay. Owing to the high-firing shrinkage of diaspore clay, most of this material is precalcined before it is incorporated in the brick batch.

Reference to Fig. 10 will show that high alumina refractories containing from 50 to 71 per cent of Al_2O_3 will, after firing, be composed of some form of SiO_2 (quartzite, cristobalite, or tridymite) and the compound mullite, $3Al_2O_3{\cdot}2SiO_2$. These also are the constituents of fire-clay brick but, as is evident from Fig. 10, the softening temperature is raised as the percentage of Al_2O_3 in a refractory is increased. A refractory containing exactly 71.8 per cent of Al_2O_3 and 28.2 per cent of SiO_2 will consist entirely of mullite, and refractories containing over 71.8 per cent of Al_2O_3 will be mixtures of mullite and corundum, Al_2O_3.

High alumina brick have found extensive application in recent years because they are more refractory than either fire-clay or silica brick. Their further application is limited only by their higher cost.

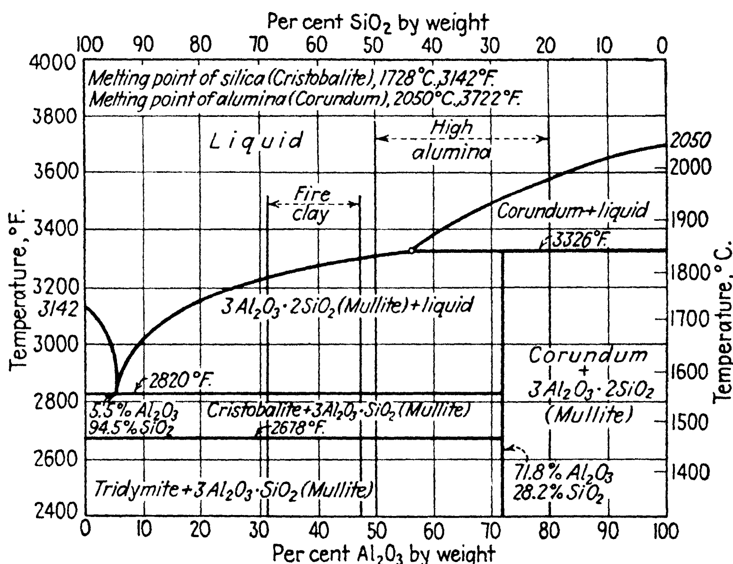


FIG. 10.—The SiO_2-Al_2O_3 temperature-composition diagram.

Silica Refractories.—Brick and other refractory materials of this class are made from a hard, dense, fine-grained quartzite known as gannister. Important deposits of this rock containing 97 to 98 per cent of silica are found in Pennsylvania, Wisconsin, and Alabama. After crushing, the rock is ground with water in a wet pan with the addition of about 2 per cent of lime, CaO. From this mixture, brick may be molded by hand, by machine, or by power presses; after drying in tunnel driers, they are fired for the proper time and at the proper temperature, either in periodic downdraft kilns or in continuous tunnel kilns. The lime serves as a strengthening bond in the unfired brick and during firing reacts chemically with some of the quartzite to impart strength to the finished product.

Most refractories undergo a shrinkage during firing. Silica brick, however, undergoes a permanent linear expansion of about 3.5 per cent during firing, owing to the allotropic transformations of quartzite to tridymite and then to cristobalite.

$$\underset{\text{sp. gr.} = 2.65}{\text{Quartzite}} \underset{}{\overset{1598°\text{F.}}{\rightleftharpoons}} \underset{\text{sp. gr.} = 2.26}{\text{Tridymite}} \overset{2678°\text{F.}}{\rightleftharpoons} \underset{\text{sp. gr.} = 2.32}{\text{Cristobalite}}$$

Thus the higher temperature forms must occupy a greater volume per unit weight than does quartzite. The transformation to the higher temperature forms normally is not complete in the firing process, and silica refractories may be expected to undergo some further permanent increase in volume while in service at high temperatures.

Silica and fire-clay refractories are used more extensively than any other types. The costs of standard silica brick and second-grade fire clay are about equal. (In 1939, standard silica brick, 9 by 4½ by 2½ in., sold for $45 per thousand.)

Magnesite Refractories.—This is the most important *basic* (page 117) refractory material. It is made by "dead-burning" the mineral magnesite which is essentially magnesium carbonate, 47.6 per cent of MgO and 52.4 per cent of CO_2. Dead-burning consists in calcining the rock at a sufficiently high temperature to drive off all CO_2 and form a dense sintered product in which the magnesia will not combine chemically with the carbon dioxide or water vapor in the atmosphere at ordinary temperatures. Dead-burned magnesite in the form of nodules or grains varying in size from very fine particles to pieces ⅝ in. in diameter may be used directly in the construction of monolithic furnace hearths (page 288) and for the preparation of "furnace magnesite" used in laying magnesite brick, or it may be used for the manufacture of magnesite brick.

Magnesite brick of three types is available: fire-bonded brick, chemically bonded brick, and "metalkase" brick. In making fire-bonded brick, carefully selected grain sizes of dead-burned magnesite are mixed with water in a wet pan, the brick are molded at high pressures in a power press, well dried in a tunnel drier, and then fired at a very high temperature. To make chemically bonded brick, a small amount of chrome ore is mixed with the dead-burned magnesite and the firing is omitted. In high-temperature service the chemically bonded brick develop characteristics that approach those of the fire-bonded magnesite. Metalkase brick are made by encasing fired or unfired magnesite in soft steel containers. If the cross section is square or rectangular, the steel casing usually covers three or four sides of the brick. In high-temperature service, the steel welds together at the heated end forming a structure that is

practically monolithic, strong, and highly resistant to spalling (page 118).

Dolomite.—The mineral dolomite is an isomorphous mixture of magnesium and calcium carbonates in approximately equal molecular proportions. When calcined it forms a mixture of CaO and MgO which is widely used to keep monolithic magnesite furnace bottoms in repair. It is not used to produce refractory bricks because the CaO will combine chemically with water and carbon dioxide in the atmosphere and cause the bricks to disintegrate.

Chrome Refractories.—Chrome ores are minerals of the spinel group[1] in which the principal consituent is $FeO \cdot Cr_2O_3$ and a minor desirable constituent is $MgO \cdot Al_2O_3$. Commercial chrome ores will contain 30 to 60 per cent Cr_2O_3; in those used as refractory materials the combined Cr_2O_3 and Al_2O_3 content will not be less than 56 per cent. The process for making chrome brick is very similar to that already described for magnesite brick. Chrome brick deserves mention as one of our most important *neutral* (page 117) refractories. Several courses of chrome brick laid between magnesite and silica brick will prevent chemical interaction between the basic magnesite and acid silica even at high temperatures.

Fosterite Refractories.—This relatively new type of refractory is coming into increased use because it will withstand higher temperatures than either fire clay or silica brick. Furthermore it possesses excellent stability and strength at high temperatures. Refractory brick of this type are made from olivine rock to which a suitable amount of magnesia is added. The chief constituent of the refractory after firing is fosterite, $2MgO \cdot SiO_2$, containing about 57.3 per cent of MgO and 42.7 per cent of SiO_2. The brick are molded by the power-press method and are fired at very high temperatures.

Refractory Mortar Materials.—Mortar materials may be classed as hot setting or air setting. Hot-setting mortars usually consist of finely ground crude or fired refractory material, or a mixture of these, of composition similar to the brick with which they are to be used. The bonding strength of these mortars depends upon a ceramic set at high temperatures. Air-setting mortars take a rigid set on drying at ordinary temperatures. Commercial materials in great variety of composition and properties are available.

[1] The spinels have the general formula $RO \cdot R_2O_3$, where RO usually is FeO or MgO and R_2O_3 may be Al_2O_3, Cr_2O_3, or Fe_2O_3.

Ceramic Bonding of Brick in Firing.—The principal object accomplished in firing brick in the process of manufacture is the development of a "ceramic bond" which imparts mechanical strength. Another object, of course, is to give the brick a "permanent set" at dimensions that will not appreciably change in service. With the exception of silica, most refractory materials undergo a considerable shrinkage on firing. The expansion during the firing of silica brick already has been discussed.

Unfired, or "green," brick consist of mixtures of particles of refractory material varying from coarse particles ¼ in. in diameter, through intermediate to very fine particles. Roughly 30 per cent of the particles would pass a 200-mesh screen. The coarse particles largely retain their identity during firing, but the ground mass of the finer particles undergoes change to form a bond between the larger particles. In some cases the bond is formed by a sintering together of adjacent grains; in other cases a certain amount of liquid forms in the ground mass at relatively low temperatures. As the temperature rises during firing, the amount of liquid increases by dissolving other materials. During the cooling cycle, the liquid serves as a medium for the formation and growth of interlocking crystals, which may constitute the bond.

Pyrometric Cones.—In practical discussions of refractories and ceramic materials, it is a common practice to speak of them as softening or fusing "at cone 15," "at cone 28," etc. These numbers refer to pyrometric, or "Seger," cones made of a series of compositions graded to possess progressively higher softening temperatures. The material to be tested is made into a cone of standard shape and compared with standard cones at standard rates of heating (150°C. per hr. for cones 022 to 20, and 100°C. per hr. for cones 23 to 38). The P.C.E. of a refractory is the number of that standard cone whose tip will touch the supporting plaque simultaneously with a cone of the refractory being tested.

Temperature end points of American pyrometric cones are given in Table 18. It must be emphasized that most refractories are not pure compounds and therefore rarely possess definite melting points. Practically all refractories will undergo plastic flow well below the temperature at which they become liquid.

The P.C.E. and approximate softening temperatures for various common refractories are given in Table 19.

Chemical Reactions of Refractories.—In many applications, the most important factor contributing to the ultimate destruction of a

refractory is the corrosion of the refractory due to its chemical interaction with its environment. The intensity of the corrosive action will depend upon the chemical composition and porosity of the refractory, the composition of the environment (slag composition, gas composition, etc.), the temperature, the amount of turbu-

TABLE 18.—TEMPERATURE END POINTS OF AMERICAN PYROMETRIC CONES

No. of cone	End point*		No. of cone	End point*	
	°C.	°F.		°C.	°F.
022	605	1121	7	1250	2282
021	615	1139	8	1260	2300
020	650	1202	9	1285	2345
019	660	1220	10	1305	2381
018	720	1328	11	1325	2417
017	770	1418	12	1335	2435
016	795	1463	13	1350	2462
015	805	1481	14	1400	2552
014	830	1526	15	1435	2615
013	860	1580	16	1465	2669
012	875	1607	17	1475	2687
011	905	1661	18	1490	2714
010	895	1643	19	1520	2768
09	930	1706	20	1530	2786
08	950	1742	23	1580	2876
07	990	1814	26	1595	2903
06	1015	1859	27	1605	2921
05	1040	1904	28	1615	2939
04	1060	1940	29	1640	2984
03	1115	2039	30	1650	3002
02	1125	2057	31	1680	3056
01	1145	2093	32	1700	3092
1	1160	2120	32½†	1722	3131
2	1165	2129	33	1745	3173
3	1170	2138	34	1760	3200
4	1190	2174	35	1785	3245
5	1205	2201	36	1810	3290
6	1230	2246	37	1820	3308
			38	1835	3335

* Pyrometric cones do not give an accurate measurement of temperature. Where it is desired to interpret P.C.E. values approximately in terms of temperature, the table above may be used. This table has been approved by the A.S.T.M. It is based on the work of Fairchild and Peters, *J. Am. Ceram. Soc.* **9**, 701–743 (1926). Heating rate 150°C. per hr. for cones 022 to 20 inclusive, and 100°C. per hr. for cones 23 to 38, inclusive. The temperatures do not apply to the slower rates of heating common in the commercial firing and the use of refractory materials.

† Not included in the tests of Fairchild and Peters. The temperatures given are approximate.

TABLE 19.—COMPOSITIONS AND PROPERTIES OF REFRACTORIES

	Fireclay			High alumina per cent, Al_2O_3				Silica	Magnesite	Chrome
	A	*B*	*C*	50	60	70	80			
Composition range (per cent):										
SiO_2	46–52	52–60	57–62	41–47	31–37	20–26	10–16	95–96	.....	3–6
Al_2O_3	43–47	34–43	31–36	47.5–52.5	57.5–62.5	67.5–72.5	77.5–82.5	.....	.....	15–33
TiO_2	2.4–2.6	2.0–2.4	1.8–2.0	2.5–2.9	3.1–3.5	3.7–4.1	4.1–4.5			
CaO	.....	.....	.....	.....	.....	.....	.....	1.8–2.5		
MgO	.....	.....	.....	.....	.....	.....	.....	.....	83–93	14–18
FeO	.....	.....	.....	.....	.....	.....	.....	.....	.....	11–17
Cr_2O_3	.....	.....	.....	.....	.....	.....	.....	.....	.....	30–45
Fe_2O_3	.....	.....	.....	.....	.....	.....	.....	.....	2.7	
Other oxides	3–4	3–6	4–7	3–4	3–4	3–4	3–4	1.5–2.5	5–10	
Specific gravity	2.65–2.75	2.60–2.70	2.55–2.65	2.75–2.85	2.90–3.05	3.15–3.25	3.35–3.45	2.30–2.40	2.30–2.40	3.80–4.10
Per cent porosity	12–16	15–24	17–21	20–25	22–30	26–31	26–31	22–30	20–28	20–28
Pyrometric cone equivalents:										
Cone	33–34	31–33	28–31	34–35	36–37	38	39	31–32	38	38
Approx. temp., °C	1745–1760	1680–1745	1615–1680	1760–1785	1810–1820	1835	1865	1680–1700	1835	1835
Approx. temp., °F	3173–3200	3056–3173	2939–3056	3200–3245	3290–3308	3335	3389	3056–3092	3335	3335
Approx. relative cost	.....	1.2	1.0	.....	.....	.....	.....	1.0	6.0–8.0	5.0–6.0

lence or agitation in the environment at the refractory surface, and other minor factors.

On a basis of chemical character of the principal oxides and compounds they contain, refractories usually are classed as *acid, basic,* or *neutral.* Thus, silica is an acidic oxide and a refractory that contains considerable uncombined silica would be classed as an acid refractory because it would react with basic slags and with gases bearing alkaline dust or vapors. On the other hand, magnesia is a strongly basic oxide and refractories composed principally of this material will react with acid slags and resist basic slags. Finally, refractories composed of oxides or compounds that have only feeble acid or base properties are classed as neutral. In general, the rate of reaction with the environment is faster for porous than for dense refractories. A classification of the common refractories is given below:

Acid refractories: Sand, ganister, and silica brick.

Neutral refractories: Chrome ore and chrome brick, fire clay and fire-clay brick, magnesium silicates (fosterite), Alundum (fused alumina), carbon and graphite, silicon carbide (crystolon or carborundum), high alumina refractories.

Basic refractories: Magnesite and magnesia brick, dolomite, lime.

Of the refractories classed as neutral, chrome ore and chrome brick best deserve the name. Alumina and high alumina refractories show basic properties in the presence of highly acid slags and also will be attacked by very basic slags. Furthermore, fire-clay refractories are attacked by highly basic slags.

When dissimilar types of refractory brick are in contact at high temperatures, they may be damaged by reacting chemically with each other. Thus, magnesite and silica brick will interact and should be separated by a course or two of neutral brick. It is common practice to use chrome brick for this purpose since chrome will not react with either. The results of a study to determine the approximate temperatures at which reactions will occur between various types of refractories are given in Table 20.

TABLE 20.—REACTION TEMPERATURES BETWEEN DIFFERENT REFRACTORIES, °C.

Type of refractory brick	Silica		Fire clay		High alumina (70% Al_2O_3)		Chrome		Magnesite	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Silica	....	....	1500	*	1600	*	No reaction		1500	1600
Fire clay	1500	*	....	....	No reaction		1600	*	1400	1500
High alumina (70% Al_2O_3)	1600	*	No reaction		....	....	1600	1600	1500	*
Chrome	No reaction		1600	*	1600	1600	....	....	No reaction	
Magnesite	1500	1600	1400	1500	1500	*	No reaction			

A. Reaction first observed. *B.* Reaction first became damaging. * Not damaging.
1400°C. = 2552°F. 1500°C. = 2732°F. 1600°C. = 2912°F. 1700°C. = 3092°F.

Before dismissing this subject, it should be mentioned that under conditions where the reaction rate between refractory and slag is

very slow, it is sometimes possible to use basic refractories with acid slags or silica brick with basic slags. These conditions usually prevail when the slag is extremely viscous or solid and forms a protective coating over the refractory surface.

Physical Factors and Refractory Behavior.—As has been mentioned, there is an upper temperature limit at which a refractory may be used because it will eventually deform plastically so easily that its strength is no longer sufficient to support the refractory structure. It should be noted, however, that a refractory may be, and regularly is, used with furnace temperatures well above the softening temperature of the refractory. Thus, fire-clay brick with a softening temperature of 2250°F. will give satisfactory service at furnace temperatures of 2600°F. or higher. The reason for this lies in the fact that a temperature gradient exists between the inner and outer faces of the brick. The hot end of the brick may be relatively soft and unable to support a load, whereas the outer portions are considerably below the softening temperature and well able to support the load of the entire refractory structure.

Although refractories are given a permanent set by firing, they still must undergo reversible expansion and contraction on heating and cooling, the amount being determined by the coefficient of thermal expansion. Linear thermal expansions for the common refractories are given in Fig. 11. The abnormal linear expansion for silica brick is due to the allotropic changes in quartz previously discussed (page 112). Proper allowance for thermal expansion must be made in the design and in the heating and cooling of refractory structures.

Spalling is defined as "the breaking or cracking of refractory brick in service to such an extent that pieces are separated or fall away, leaving new surfaces of the brick exposed." Frequently operating conditions of necessity expose refractories to spalling influences, but much can be done to minimize spalling by proper design of brick shapes, and by proper design, construction, and operation of the furnace.

Thermal spalling is caused mainly by the rapid expansion or contraction of the brick due to rapid temperature changes. High-grade fire-clay brick probably has the highest resistance to thermal spalling of the common refractories. Silica brick is especially susceptible to rapid temperature changes below a dull-red heat, because of the abrupt volume change accompanying the allotropic transformation. At higher temperatures (above 1120°F.), however,

silica brick has good resistance to rapid temperature changes. Fire-clay and high alumina brick have a high, and magnesite and chrome brick a low, resistance to thermal shock.

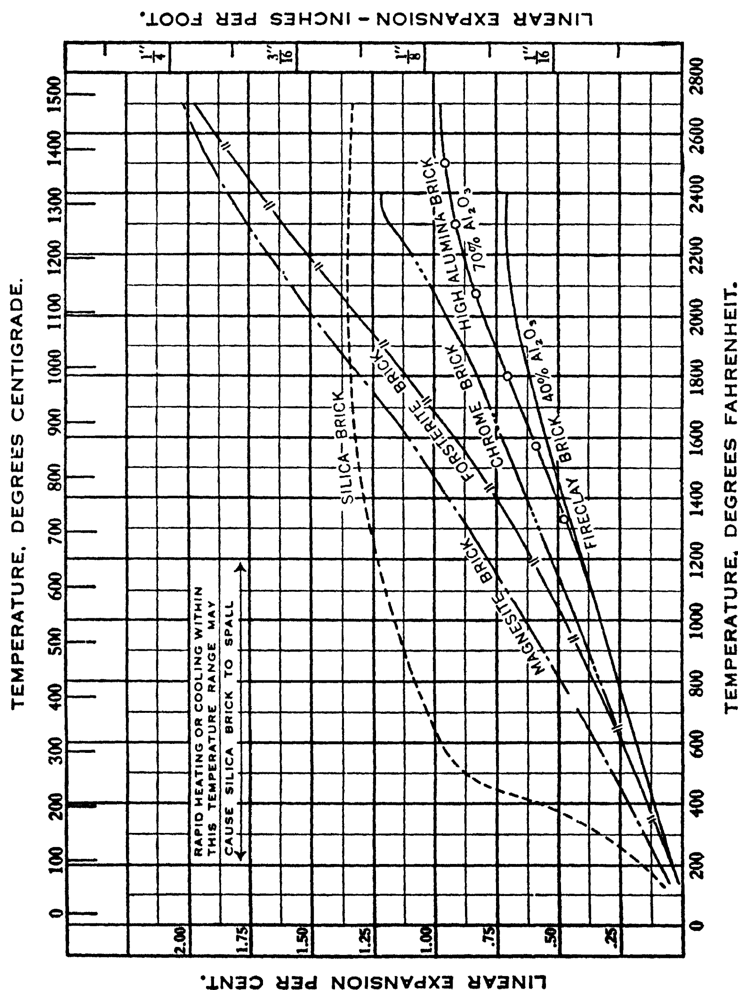


FIG. 11.—Linear thermal expansion of refractories. (*From "Modern Refractory Practice," Harbison-Walker Refractories Company.*)

Mechanical spalling frequently results from lack of care in the removal of slag and clinker from refractory surfaces or from "pinching" in sprung arches which results in concentrating the arch stresses on a relatively small bearing surface at the hot end of the brick. External insulation to decrease the temperature gradient through arch brick tends to reduce "pinch spalling."

Structural spalling results from changes in composition of the brick from the hot to the cold end during service, resulting in zones of different strengths and expansion coefficients. In silica brick these zones may develop owing to the fact that different forms of silica are stable at the temperatures that prevail in the separate zones. With other brick, and also with silica brick, zones of different composition and properties may develop owing to the absorption of slags or fluxes or to reaction of the hot end of the brick with reducing or oxidizing gases.

An interesting effect of carbon monoxide and partly cracked natural gas on refractory brick should be mentioned. Under proper conditions of temperature and gas composition, these gases may deposit carbon within the pores of the brick, so weakening its bond that it will disintegrate. This effect is most noticeable in the temperature range 420 to 470°C. (790 to 880°F.). The bond in brick also may be weakened by contact with such gases as chlorine, hydrogen chloride, and sulfur dioxide.

Erosion and Solution of Refractories.—When hot, dust-bearing gases at high velocities impinge upon refractories, there is considerable erosion. This effect is particularly noticeable at the arches and outgoing ports of furnaces. When molten metals flow over refractory surfaces, the refractory is gradually eroded. The erosion of the nozzles of teeming ladles and the linings of furnace runners in the steel plant provide excellent examples. Finally it should be mentioned that refractories may be appreciably attacked by slags without chemical reaction if the refractory has true solubility in the slag and the slag is in motion.

Thermal Conductivity and Specific Heat of Refractories.—A high thermal conductivity is desirable for refractories used in retorts, muffles, by-product coke-oven walls, and recuperators. In most furnaces, however, a low thermal conductivity is desirable or necessary to conserve heat and to attain the required temperature. When the desired refractoriness and thermal resistance cannot be obtained in a single refractory, it is common practice to construct a furnace with brick of the desired refractory properties on the inside and brick of low thermal conductivity on the outside of the wall, hearth, or roof. The thermal conductivities of some common refractory brick are given in Fig. 12.

For convenience in estimating the heat that must be put into refractories to raise them to a given temperature, the mean specific

heats between 32 and t°F. for common varieties of brick are given in Fig. 13.

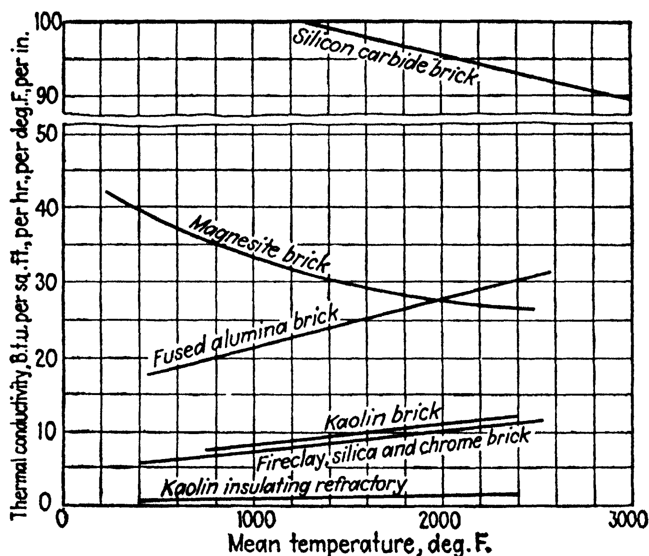


FIG. 12.—Thermal conductivity of refractories.

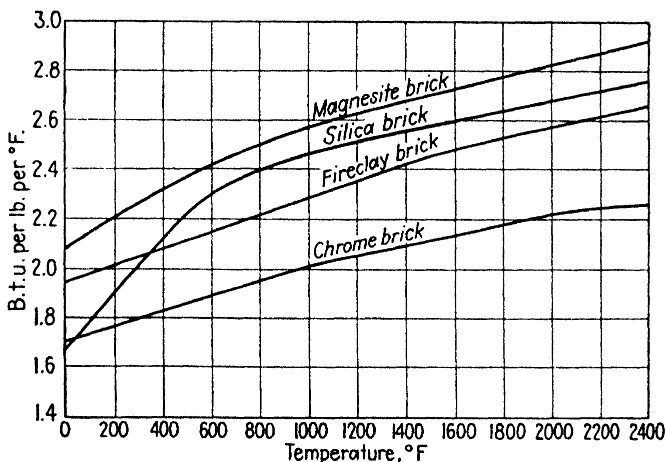


FIG. 13.—Mean specific heats of refractories between 32°F. and t°F.

Refractories of Minor Importance.—There are a number of metal oxides that have excellent refractory properties but are limited to laboratory and other special uses because of their high cost. Among these may be mentioned *thoria*, ThO_2, (m.p. above

2800°C.), *zirconia*, ZrO_2 (m.p. about 2700°C.), and *beryllium oxide*, BeO (m.p. about 2450°C.). All these would be classed as inert or neutral refractories. *Zirconium silicate*, melting at about 2500°C., is an excellent neutral refractory.

Carbon, especially in the form of *graphite*, with a melting point above 3500°C., is very refractory and is neutral to acids and bases. It is strongly reducing, however, and must be used in a reducing environment. Graphite finds considerable use when mixed with a clay binder in the manufacture of crucibles for metal melting. *Silicon carbide* dissociates at about 2240°C., before its melting point is reached. It has reducing properties and is rather rapidly attacked by fused acid, basic, or neutral slags. It is quite satisfactory in contact with hot gases at high temperature unless the gases are strongly oxidizing. It has been used in place of graphite in the manufacture of crucibles and in the construction of high-temperature recuperators or heat exchangers.

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"Modern Refractory Practice," Harbison-Walker Refractories Company, Pittsburgh, Pa. (1937).

NORTON: "Refractories," McGraw-Hill Book Company, Inc., New York (1931).

CHAPTER IV

THE NONFERROUS METALS

By Harry Seltz, Ph.D.

We are living today in a "metal age." Some idea of the vastness of the metal industries can be had from the figures for yearly world production of all metals from their ores. This figure is greater than 300 million tons. The value of these metals is enormous. The pig iron produced per year has alone a value close to 2 billion dollars, and the copper produced a value of nearly half a billion. Of the 92 elements of the periodic system, 70 are classed as metals, and about 30 of these have industrial uses. Of these 30, however, iron accounts for more than 90 per cent of the total tonnage production. For this reason it is customary to discuss iron and its alloys separately (Chaps. VI and VII) and to treat the others under the heading of nonferrous metals. The more important nonferrous metals are listed in Table 21 with approximate annual

Table 21.—Yearly Production of Metals (1937)

Metal	Metric Tons*
Copper	2,600,000
Lead	1,900,000
Zinc	1,800,000
Aluminum	550,000
Tin	210,000
Nickel	115,000
Antimony	38,000
Tungsten	32,000
Magnesium	18,000
Molybdenum	16,000
Silver	8,000
Mercury	4,000
Cadmium	4,000
Cobalt	3,000
Vanadium	2,000
Bismuth	2,000
Gold	1,000

* Figures on world production of Mn, Cr, and Ti are not available.

world production[1] in tons. Of these metals Al, Cd, Cu, Au, Pb, Mg, Hg, Mo, Ni, Ag, Zn, W, and Sn are used in considerable quantities in the pure state or as the principal constituent of alloys. Sb, Bi, Cr, Co, Mn, and Ti are used essentially as minor constituents of alloys. A great number of mixtures of nonferrous metals give rise to extremely important alloys, some of which will be discussed in the next chapter.

Properties of Metals.—Metals, both pure and as alloys, have the most diversified applications, in which their physical and mechanical properties must meet exacting requirements. It is, therefore, advisable to define some of the more important physical and mechanical properties and to describe the measurements and tests that are made to determine the fitness of a metal for a particular application.

Physical Properties

The *melting or freezing point* of a pure metal is defined as the temperature at which the solid and liquid phases can exist in stable equilibrium. When a metal is heated to its melting point, the liquid phase appears and, if more heat is supplied, the solid melts completely at constant temperature. The freezing of a pure liquid, on the other hand, may exhibit the phenomenon of supercooling; the liquid in some cases can be lowered appreciably beyond the melting point without the appearance of crystals. However, when the crystals do appear, the mass rapidly assumes the normal temperature of the melting point. A wide range of melting points is found among the nonferrous metals just listed and their uses may be influenced thereby. The use of mercury in thermometers, manometers, and other instruments arises from its low melting point; the use of tungsten filaments in incandescent light bulbs is possible because of its extremely high melting point.

The *boiling point* of a liquid is the temperature at which its vapor pressure is equal to one atmosphere. The boiling points of the metals, except mercury, are high. The boiling points of zinc (907°C.) and cadmium (865°C.) are sufficiently low so that in the recovery of these metals from their ores the metals are vaporized and recondensed.

The *density* of a substance in the metric system is stated in grams per cubic centimeter and in the English system in pounds per cubic

[1] "Minerals Yearbook, 1938," U.S. Bureau of Mines.

foot. The low densities of aluminum and magnesium and of their alloys make them particularly valuable in aeronautic and transportation construction.

The *linear coefficient of expansion of a solid* is defined as the increase in length, per unit length, for each degree rise in temperature. If the temperature scale is centigrade, the value of this coefficient is 9/5 the value of the Fahrenheit scale. These coefficients are important when metals are to be exposed to a considerable range of temperatures as in engine pistons and other accurately fitting mechanisms.

The *thermal conductivity* of a metal must be considered in any application that involves either the transmission of heat or heat insulation. The rate at which heat is conducted through a metal depends on the temperature gradient and on the cross-sectional area. The "thermal conductivity" in c.g.s. units is thus defined as the number of calories of heat that would flow per second through a specimen 1 sq. cm. in cross section and 1 cm. in length when the temperature gradient is 1°C. Silver and copper show the highest thermal conductivity of all metals. Some metal alloys like German silver (page 239) exhibit very low conductivities and hence find applications where heat losses by metallic conduction should be kept to a minimum.

All metals are conductors of electricity; silver is the best conductor and copper is next. It should be noted that, while *volume for volume* aluminum has only 61 per cent of the conductivity of copper, nevertheless *weight for weight* aluminum, because of its low density, shows a conductivity nearly twice that of copper. The resistance of a metal is the reciprocal of its conductivity, and this is the property which is most commonly defined. The *electrical resistivity* of a metal is the resistance of a specimen 1 cm. in length and 1 sq. cm. in cross section. Since these values for metals are very small if expressed in ohms, they are usually given in microhms, where 1 microhm = 10^{-6} ohm.

The values of these various physical constants for the metals will be given under the discussion of their properties in the text.

Mechanical Properties of Metals

In deciding the fitness of a metal or alloy for a particular use, it is necessary to consider certain of its mechanical properties. Some of these properties, along with the methods of testing, will now be discussed briefly.

Tensile Strength.—When a force applied to a metal tends to elongate it, the specimen is said to be under tension, and stresses are produced in the metal that tend to resist the change in length.

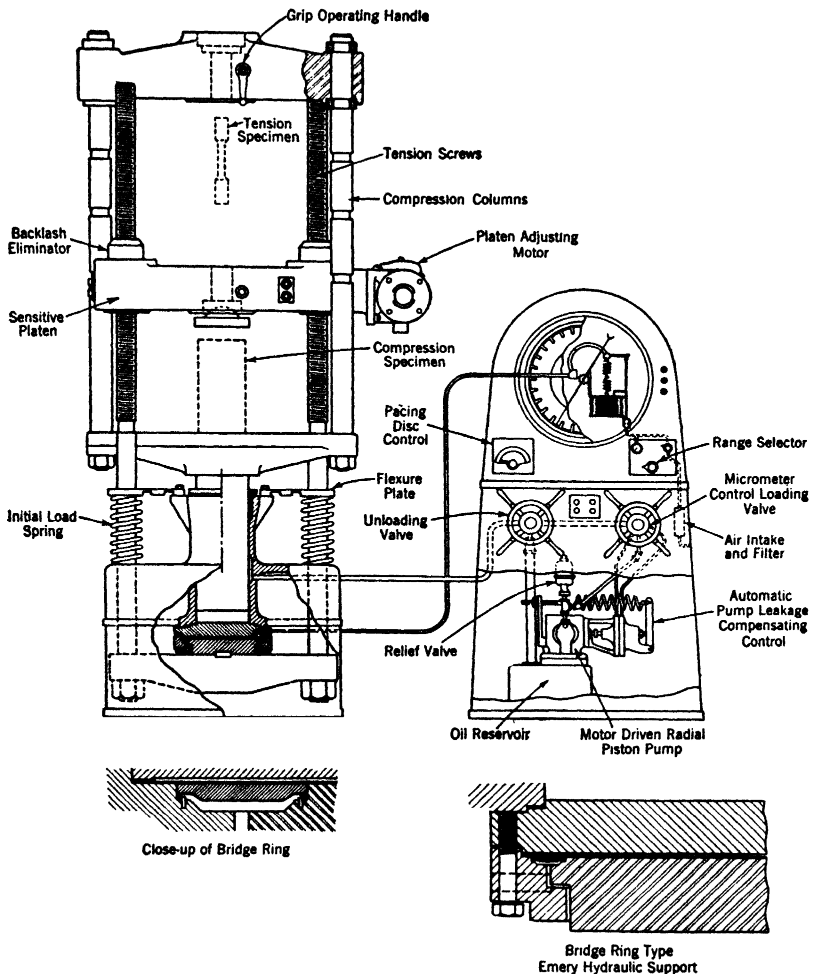


FIG. 14.—The Southwark-Tate-Emery testing machine. (*Courtesy of the Baldwin Southwark Division of the Baldwin Locomotive Works.*)

These stresses are defined in force per unit area, usually in pounds per square inch (psi). The tensile strength of a metal is the maximum stress developed when the tension is carried to the point of rupture of the metal. It is calculated by dividing the maximum load applied by the original cross-sectional area of the specimen.

When testing nonbrittle materials in tension, it is found that the specimen shows a local constriction at the point of fracture. The value obtained by dividing the decrease in area by the original area of cross section at the point of fracture, when expressed in per cent, is called the *reduction of area.* After breaking in tension, the two pieces of the test specimen are fitted together, and the increase in length of the specimen is measured. The increase in length

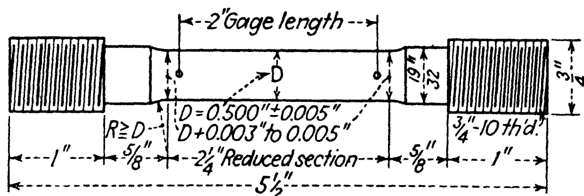


FIG. 15.—Specimen for tensile test.

divided by the original length of the part of the specimen that was rendered liable to stretching furnishes a value which, when expressed in per cent, is called *elongation.* The tougher the material, the greater the elongation. Special testing machines (Fig. 14) are available for the determination of tensile strength, and standardized forms of test specimens are used (Fig. 15). The approximate tensile strengths of some of the nonferrous metals are given in Table 22.

It is important to note that the structure of a metal may markedly affect its tensile strength and other mechanical properties. A single crystal of a metal will have a definite and characteristic tensile strength, but an ordinary piece of metal is composed of a great number of small crystalline units, variously arranged, called *grains.* Cold working of a metal by drawing it into wire, hammering, or rolling may decrease the grain size and materially increase the tensile strength, as shown in Table 22.

Modulus of Elasticity, Elastic Limit, Yield Strength.—When a tensile load is applied to a specimen, an increase in length occurs. Within certain limits, on removal of the load the specimen returns to its original length. The increase in length, per unit length, is called the strain. With metals it is found that the *ratio of stress to strain* over a considerable range is constant. This is known as *Hooke's law,* and the numerical value of this constant ratio, in pounds per square inch, is called the *modulus of elasticity* of the metal. If tensile loading is continued, a point is finally reached at which the ratio of stress to strain begins to decrease and the increase

in length is no longer proportional to the loading. The stress at which this departure from Hooke's law occurs is called the *proportional limit* of the metal. When this limit is exceeded, it is found that on releasing the load the specimen does not return to its original length; permanent deformation has occurred. The greatest stress that a metal is capable of achieving without permanent

TABLE 22.—TENSILE STRENGTHS OF METALS

Metal	Tensile strength, psi	Remarks
Tungsten	590,000	
Molybdenum	260,000	
Nickel	65,000– 75,000	Rolled and annealed
	120,000–140,000	Hard rolled
Cobalt	33,000	Cast
	63,000	Hard drawn
Copper	31,800	Commercial, rolled and annealed
	60,000	Hard drawn
Silver	40,000	Cast
	51,000	Hard drawn
Gold	20,000	Cast
	37,000	Hard-drawn wire
Magnesium	13,000	As cast
	25,000	Rolled
Zinc	16,000– 19,000	Wrought
Cadmium	13,500	
Aluminum	8,500	Pure (99.97%) annealed
	13,000	Commercial (99.4%) annealed
Lead	2,765	Commercial
	1,600	Very pure
Tin	2,000	

deformation is called the *elastic limit.* For metals the elastic and proportional limits are practically identical. It is quite difficult to determine the exact point at which permanent deformation begins. For this reason another term frequently used in testing metals is the *yield strength,* or the *yield point.* This is the stress at which a metal exhibits a specified permanent increase in length, commonly 0.5 per cent. The conventions used in defining yield points vary for different metals and alloys. For a detailed description the reader is referred to the A.S.T.M. Standards.

Besides tension testing of metals, compression and torsion tests are important in some applications of metals. Methods of measur-

ing the mechanical characteristics under compression and torsion loading are described in more detailed treatises.[1]

Hardness.—One of the most important properties of metals is that which is broadly called hardness. This property is difficult to define and impossible to measure on any absolute scale. It might be defined as the resistance that a substance offers to the separation of its particles by the penetrating action of another substance. However, there are other kinds of hardness, such as the hardness associated with the resistance to cutting and abrasion. There are several standard testing devices for determining the relative hardness of metals, of which only three will be described here. In the *Brinell* test the specimen is indented by a hardened steel ball, usually 10 mm. in diameter, under a standard load of 500, 1,000, or 3,000 kg. The ratio of load in kilograms to the total area of the indentation is called the Brinell hardness number of the material. The area of the indentation can be found in tables[2] where the area is tabulated relative to the diameter of the imprint which is readily measured.

The *Rockwell* hardness test measures the depth of penetration of a specimen by a steel ball or a diamond cone under a fixed load. In using this instrument, the penetrator is first set in the metal by applying an initial small load of 10 kg. The graduated dial is then adjusted to the "set" position and the major load,[3] whose value depends on the nature of the specimen, is applied. When the pointer of the instrument comes to rest, the major load is removed and an inverse scale reads the hardness number directly.

The *scleroscope* test uses the rebound of a diamond-tipped hammer from the surface of the metal specimen as a measure of the hardness. The hammer drops, under the force of gravity only, from a fixed height and the rebound from the test specimen is measured by a recording dial on the instrument.

Fatigue.—Another mechanical test that has become very important in recent years is the *fatigue test*. It has been found that when metals are subjected to repeated reversals of stress, even though the maximum stress does not exceed the elastic limit, they may eventually fail if the stress cycles on the specimen are suffi-

[1] JEFFRIES and ARCHER, "The Science of Metals," McGraw-Hill Book Company, Inc., New York (1924).

[2] Furnished by the manufacturer of the instrument.

[3] CAMP and FRANCIS, "Making, Shaping and Treating of Steel," 5th ed., pp. 562–573, Carnegie-Illinois Steel Corp., Pittsburgh, Pa. (1940).

ciently numerous. Studies of fatigue have greatly increased our knowledge of the safe operating conditions for structural parts of machines that are subjected to dynamic loads.

Ductility.—If a metal resists rupture when greatly extended in tension, it is said to be ductile. It is by virtue of this property that a metal may be drawn into a wire. To be formed in this manner, a metal must show considerable tensile strength after great deformation. Lead, for example, although readily deformed, cannot be drawn into wire because of its low tensile strength.

Malleability.—This is the property by virtue of which a material may be hammered or rolled into thin sheets without rupture. This property generally increases with increase of temperature.

Table 23 lists the common metals in the order of their ductility and malleability at room temperature.

TABLE 23.—METALS IN ORDER OF DUCTILITY AND OF MALLEABILITY

Ductility	*Malleability*
Gold	Gold
Silver	Silver
Platinum	Copper
Iron	Aluminum
Nickel	Tin
Copper	Platinum
Aluminum	Lead
Zinc	Zinc
Tin	Iron
Lead	Nickel

In the discussion of the nonferrous metals in the following pages of this chapter and of the nonferrous alloys in the next chapter, their important mechanical characteristics will be described.

ALUMINUM

Historical.—Aluminum was a rare metal as late as 1850, and it was not produced commercially until 1889; nevertheless, among the nonferrous metals, it is now outranked by only copper, lead, and zinc in annual output. The metal was first isolated in 1825 by Oersted, who reduced aluminum chloride with potassium amalgam. In 1827 Woehler repeated Oersted's experiment without success, but by modifying the procedure slightly he obtained the metal in the form of a gray powder. Eighteen years more elapsed, however, before Woehler produced the metal in a form pure enough to determine its properties. In 1855 the price of aluminum was $113 a pound. In 1886 Hall in America and

Heroult in Europe, working independently, developed an electrometallurgical method, which by 1890 brought the price to $2.38 a pound. By 1900, it had dropped to 23 cts. and in 1914 the lowest price, 18 cts., was reached.

Hall's discovery was made when he was twenty-three years old, the year following his graduation from college. Without being aware of Hall's work, Heroult, a Frenchman, also twenty-three years of age, discovered the same process exactly 3 months later. Although the processes were practically identical, there was no patent litigation. In America, Hall's company began operations at Pittsburgh and later moved to New Kensington, Pa.

Occurrence.—Of all the metals, aluminum exists in the outer layer of the earth in the greatest quantity. Indeed, among all the elements it is exceeded only by oxygen and silicon. It makes up about 8 per cent of the earth's crust, while the total quantity of iron amounts to slightly more than 5 per cent. The other common metals, as copper, lead, zinc, and tin, taken together constitute only a small fractional part of 1 per cent of the exterior portion of the earth. Aluminum oxide, called *alumina,* which when pure is white in color, is an essential ingredient of such mineral as clays, slates, mica, feldspar, and granite. Alumina forms several precious stones.

Corundum consists of anhydrous alumina. The ruby is made up of crystals of corundum colored red by a small amount of chromium. The sapphire is another variety, colored blue by small traces of cobalt. Emery is an impure variety of corundum containing ferric oxide. It has a granular structure and a degree of hardness only a little less than that of the diamond. Because of its hardness, it is used as an abrasive material (page 513).

Ores.—Although aluminum is very abundant in the earth, it is never found free, nor can it, by present methods, be obtained commercially from clay in which it exists in such great quantities. There is but one commercial ore, called bauxite. It takes its name from the village of Baus, near Arles, in France, where it first was found by Berthier. Bauxite is a hydrated aluminum oxide, generally believed to consist of a mixture of the monohydrate $Al_2O_3 \cdot H_2O$ and the trihydrate $Al_2O_3 \cdot 3H_2O$.[1] The chief impurities are iron oxides, silica, clay, and titanium dioxide. Depending upon the iron-oxide content, the color varies considerably. Its structure is

[1] EDWARDS, FRARY, and JEFFRIES, "The Aluminum Industry," Vol. I, p. 63, McGraw-Hill Book Company, Inc., New York (1930).

variable also; usually it is made up of rounded concretionary grains imbedded in a claylike mass.

The chief deposits of bauxite now being worked are located in Italy, France, British and Dutch Guiana, and the United States, where the chief producers are Arkansas, Alabama, Georgia, and Tennessee. Formerly the best ore was obtained from France, but the vast deposits in the Guianas, controlled by an American company, have proved to be purer than the French ore. An extensive deposit of very high grade has recently been discovered in the Atlas Mountains in French Morocco.

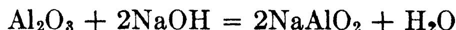
Cryolite.—The fluorides are the only aluminum-bearing minerals in which the metal is not associated with oxygen. Cryolite, a sodium aluminum fluoride, $3NaF \cdot AlF_3$, is required in aluminum metallurgy as solvent for the bauxite. It is a white, icelike solid, melting at 995°C. The deposit at Ivigtut, in southern Greenland, is the only commercial source of cryolite. Owing to the high price of the native mineral, methods of preparing cryolite artificially have been developed.

Production of Aluminum.—Because an enormous amount of electric energy is required (about 10 kw.-hr. per lb. of metal), and because it must be supplied at low cost, all the aluminum-reduction plants in the world derive their current from hydroelectric power plants. This fact causes the reduction plants to be located in the general vicinity of waterfalls. Power from coal is out of the question. Aluminum ores, consequently, are usually not smelted where mined. Arkansas, for example, of all the states, is the greatest producer of bauxite, but the state of New York leads in the production of aluminum. The ore is mined in Arkansas, is refined in St. Louis, and is smelted not far from Niagara Falls where power is cheap. The bauxites found in the United States, as a rule, contain from 15 to 33 per cent of water of hydration, with additional moisture mechanically held, and because ordinarily the ore must be shipped long distances, it is usually dried at the mine.

One of the problems encountered in aluminum metallurgy arises from the fact that after reducing to the metallic state, the metal can be refined only with difficulty. As a result, before reduction is started, it is necessary to prepare an alumina that is essentially pure. The purity of the metal depends upon the purity both of the oxide reduced and of the fused bath of cryolite.

In the process now usually employed in preparing the alumina, known as the Bayer process, the finely ground ore is digested in

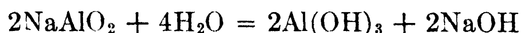
an aqueous solution of sodium hydroxide under pressure in steam-jacketed autoclaves. Sodium aluminates are formed, as illustrated by the following equation:



$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O$$

The ferric oxide, clay, and titanium dioxide are not dissolved. Part of the silica dissolves, but this is precipitated as calcium silicate by the use of lime which was added to the ore for this purpose prior to grinding.

The sodium aluminate liquor from the autoclaves is diluted, filtered, and run into tanks. A small amount of freshly prepared aluminum hydroxide is added to the liquor to act as a "seeding" agent and the sodium aluminate decomposes and precipitates aluminum hydroxide, as follows:



$$2NaAlO_2 + 4H_2O = 2Al(OH)_3 + 2NaOH$$

The aluminum hydroxide sludge from the bottom of the tank is drawn off and put through filter presses. Afterward, the hydroxide is calcined[1] to alumina. The sodium hydroxide solution is concentrated by evaporation and is used again.

The reduction of aluminum oxide to aluminum by means of carbon, as is done in the case of iron, copper, lead, tin, and other commercial metals, is not practicable. Although the alumina can actually be reduced, under the conditions required for the reduction, the metallic aluminum undergoes secondary reactions. It will form the carbide by combining directly with carbon, will form the oxide or carbide by reacting with carbon monoxide or dioxide, or will volatilize. If some other metal, such as copper, is present with which the aluminum can form an alloy as it is reduced, reduction with carbon may be employed. Pure aluminum, of course, cannot be obtained in this way. In 1886, and for several years thereafter, until driven from the field by Hall process, the Cowles brothers successfully prepared aluminum alloys on a commercial scale by the carbon reduction method.

In the Hall process, now almost exclusively used, the furnace employed consists of a rectangular box of mild steel lined with refractory material possessing low thermal and electric conductivity.

[1] To *calcine* means to heat strongly to drive out volatile matter, as carbon dioxide and water, leaving a friable product. The manufacture of lime by heating limestone is a calcining process.

Inside this lining is another of rammed carbon to form a cathode, electrical contact with which is made by a suitable lead (Fig. 16). Anodes of hard-pressed carbon are suspended in the interior of the furnace.

The bath consists of melted cryolite, both natural and artificial, to which other salts, such as calcium fluoride, have been added. Since the specific gravity of melted aluminum and the melted bath are not far apart, care must be exercised to adjust the composi-

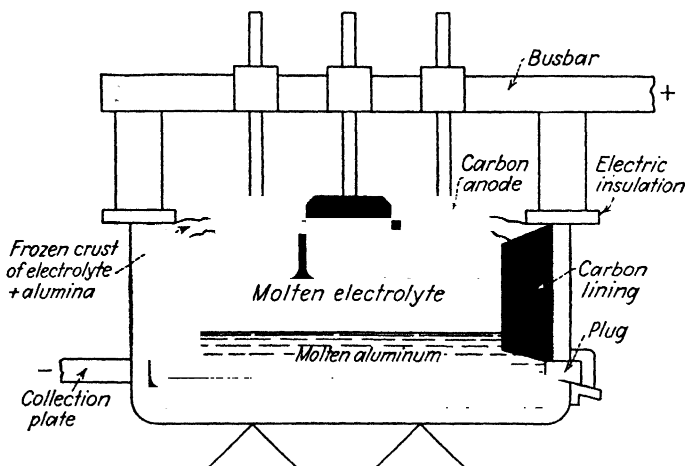


Fig. 16.—Electrolytic cell for production of aluminum.

tion of the bath so that the reduced aluminum does not float; if this should happen, the cell would be short-circuited. The melting point is also a factor to be considered in adjusting the composition. In the bath of fused salts the purified alumina is dissolved in a quantity varying from 10 to 20 per cent. During the electrolysis, aluminum separates at the cathode and oxygen is evolved at the carbon anodes.

The separated aluminum collects on the cathode bottom, which slopes slightly toward the tap hole; periodically the metal is tapped. The oxygen reacts with the hot carbon anode to form carbon monoxide, which burns to the dioxide as it escapes. From time to time, cryolite and alumina are added to replenish the bath.

Commercial Aluminum.—The product of the reduction cell is remelted in order to allow occluded bath salts to separate, and then is cast in pigs. In this form it appears on the market as primary aluminum, of which there are three grades, as follows:

Classification	Per Cent of Aluminum
1. Special	99.5+
2. Grade No. 1 (or Grade A)	99.0+
3. Grade No. 2 (or Grade B)	98 to 99

The 99+ aluminum contains on an average the following impurities: copper, trace to 0.20; iron 0.25 to 0.60; and silicon, 0.15 to 0.40 per cent. A small amount of the oxide, Al_2O_3, is also normally present in commercial aluminum.

Pure Aluminum.—The purity of the aluminum produced by the Hall process does as a rule not exceed 99.5 per cent; with other metals, such as copper, zinc, and tin, a purity as high as 99.95 per cent has long been common. Because of its peculiar chemical and metallurgical behavior, it seemed that commercial aluminum could not be refined, but recently the Hoopes electrolytic refining cell, yielding a product having a purity as high as 99.97 per cent, has come into use on a commercial scale.

In this process a layer of heavy, molten alloy of aluminum, copper, and silicon is employed in the bottom of the cell as the anode. This melted anode is covered with a layer of fused electrolyte consisting of the fluorides of sodium, aluminum, and barium. Above the electrolyte is a cathode layer of pure, melted aluminum. The layers float one above the other and remain separated because of their differences in density. An electric current passing through the cell removes aluminum from the anode alloy and deposits it with the pure aluminum of the cathode.

Pure aluminum does not cast very well. When molten it absorbs nitrogen, carbon dioxide, etc.; when these gases are expelled again on cooling, they form gas flaws. Small additions of copper, nickel (page 240), and some other metals improve the casting qualities of the metal in this respect. Because aluminum has a tendency to be coarsely crystalline, the temperature of the melted metal in casting should be as low as practicable in order to keep the crystalline structure as fine as possible. The fine crystals increase the tensile strength. Aluminum shrinks upon solidifying from the melted state 0.2031 in. per ft. Its casting alloys (page 241), which contain about 8 per cent of copper, shrink somewhat less than this, about 0.156 in. per ft.

By the fusion process, aluminum and its alloys may be welded. In this process the fluxes generally used are mixtures of salts, such as the fluorides, chlorides, and sulfates of potassium, sodium, lithium, calcium, and aluminum. For use, the salts are mixed with

water to form a thin paste.[1] Since all successful aluminum fluxes are corrosive to the metal, the flux must be completely removed after welding. According to the reference just given, this may be accomplished by washing first in hot water and then in a 5 per cent solution of either nitric or sulfuric acid, after which the acid must be removed by washing again in clean hot water.

Physical and Mechanical Properties.—Pure aluminum has a silvery color and luster, while the commercial grades show a characteristic bluish tinge. The high purity metal has a much greater resistance to corrosion than the ordinary metal. Edwards reports that a sample of 99.9 per cent aluminum sheet kept in a solution consisting of 5 parts by volume of concentrated hydrochloric acid and 95 parts of water was still bright and showed no appreciable corrosion after six weeks. Ordinary polished aluminum sheet in this solution dissolves sufficiently to show a decided hydrogen evolution in a few minutes, and is distinctly etched in one hour. Aluminum is ductile and malleable (Table 23); it may be rolled into sheets 0.0005 in. in thickness. Its density is the lowest of all metals that are permanent in air, having about one-third the density of steel. In proportion to its weight, it is quite strong. The properties of the metal are summarized in Table 24.

TABLE 24.—PHYSICAL AND MECHANICAL PROPERTIES OF ALUMINUM

Melting point	658.6°C. (1217.4°F.)
Boiling point	2057.°C. (3734.°F.)
Density	2.703 g. per cc., at 20°C.
Electrical resistivity	2.669 microhms per cm.^{3}, at 20°C.
Thermal conductivity	0.5 c.g.s. units
Tensile strength	9,000 psi
Modulus of elasticity	10^7 psi
Hardness	15 Brinell (500 kg. load, 10 mm. ball)

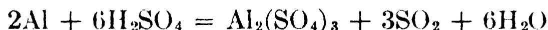
Chemical Properties.—When strongly heated in the air, aluminum oxidizes considerably. Thin pieces will burn in the air with a brilliant light, resembling magnesium; aluminum oxide and some nitride are formed. In casting, however, it is not necessary to cover the metal with charcoal, because the tenacious film of oxide that is formed is protective. Zinc chloride, which melts at 365°C., is the best flux for aluminum.

Upon exposure to the ordinary atmosphere, aluminum corrodes very slowly; a thin film of the hydrated oxide is formed, which is closely adherent and protective. If it were not for this protecting

[1] EDWARDS, FRARY, and JEFFRIES, *op. cit.*, Vol. II, p. 440.

film, the metal would be rapidly attacked. When amalgamated with mercury, aluminum dissolves readily in pure water with the formation of aluminum hydroxide and the evolution of hydrogen. In warm, moist air the aluminum hydroxide grows out from the metal in a form like moss; it may reach a length of nearly a half inch in a very short time. The amalgamation does not increase the activity of the aluminum; it prevents the formation of the protective film that usually interferes with its activity. Hydrogen sulfide has no action on aluminum.

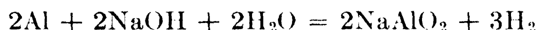
Aluminum is practically unaffected by dilute sulfuric acid, but the concentrated acid dissolves it readily, with the evolution of sulfur dioxide:



$$2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

Nitric acid also affects it very little. Aluminum may be employed for handling cold nitric acid, both dilute and concentrated. It is attacked very rapidly by both hydrochloric and hydrofluoric acids in all concentrations with the evolution of hydrogen. Chlorine, bromine, and iodine all attack aluminum rapidly. With elementary sulfur, aluminum reacts readily at moderately high temperatures; the sulfide, Al_2S_3, is formed. Aluminum sulfide is not formed in the wet way by reacting with a solution of hydrogen sulfide.

In solutions of the caustic alkalies, the metal dissolves very readily. The products formed are hydrogen and aluminates:



$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

Hence, solutions of the alkalies, such as caustic soda, should not be used in cleaning articles made of aluminum. The presence of a small quantity of sodium silicate inhibits the action of alkalies on this metal.

Uses of Aluminum.—Because of its softness and the difficulty of making sound castings, little pure aluminum is used in the cast form. The largest quantity is employed after it has been mechanically worked in some manner, as by rolling, wire drawing, drop forging, or extruding. After being rolled into sheets, it may be stamped into a variety of shapes. It is employed, often alloyed with smaller amounts of other metals (page 244), in the manufacture of furniture, airplanes, railroad and trolley cars, automobile bodies and pistons, electric cables and bus bars, rigid conduits, rivets, kitchen utensils, and collapsible tubes for pastes. Aluminum shingles, corrugated roofing and siding sheets, and Mason-jar caps are recent products

that seem to have been well received. To summarize its mechanical uses, it may be said that aluminum is employed wherever advantage may be taken of its low density, relatively high combined strength and toughness, or its high electrical and thermal conductivity. When employed because of its lightness, if more than its normal strength is also required, this may be secured by the use of aluminum alloys (page 239).

In a finely divided flake form, aluminum is employed as a pigment in paint (page 558). Aluminum paint is used as a priming coat for wood and as a protective coat for metals. For the latter purpose it is exceptionally serviceable.

Aluminum is used in deoxidizing molten iron and steel, especially in the top of the ingot when steel is poured in the ingot mold. In a similar manner it is used to prepare the metals from their oxides by heating a mixture of powdered aluminum and the oxide of the metal to be reduced. The mixture is known as Thermit.

The application of aluminum in the United States shows the following distribution:[1]

	Per Cent
Transportation	38
Electrical conductivity	16
Cooking utensils	14
Machinery and electrical appliances	9
Metallurgy of iron and steel	8
Building construction	4
Chemical	2
Miscellaneous	9

Thermit.—Finely divided aluminum is mixed with the metallic oxide in about equal proportions by volume. When the reaction between the two is started, it proceeds of itself and develops great heat; the products are a slag of aluminum oxide and the molten metal whose oxide was reduced. The reaction is started in the Thermit by means of a small quantity of ignition powder placed on top of it. The ignition powder is made up of a mixture of barium peroxide and finely divided magnesium, and reacts according to the following reaction:



$$BaO_2 + Mg = BaO + MgO$$

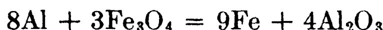
In the Thermit itself, if ferric oxide is used, the reaction is as follows:

[1] EDWARDS, "Metals Handbook," American Society for Metals, Cleveland, (1936).



$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

The mixture of ferric oxide with aluminum is known as "red Thermit" and the magnetic oxide as "black Thermit"; the latter is probably the most used. The reaction with the magnetic oxide occurs thus:



$$8Al + 3Fe_3O_4 = 9Fe + 4Al_2O_3$$

From this equation, the theoretical weights are approximately 3 of aluminum and 10 of magnetic oxide, which produce about 7 of metallic iron and 6 of slag. In actual practice the proportions are usually 1 of aluminum and 3 of magnetic oxide. It is generally estimated that the molten metal produced is about one-half the original mixture by weight and about one-quarter by volume.

The temperature produced by the heat of the Thermit reaction is very great. It has been calculated by Richards as 2694°C. Fery, using the radiation pyrometer, found the temperature of the stream of metal flowing from the crucible to be 2300°C.

The exceedingly hot metal has proved to be very useful in a certain form of welding. For the purpose of welding, the parts to be joined are cleaned, butted together, and the joint is surrounded by a suitable mold. The ends are then heated by a gas flame playing through an opening provided in the mold for this purpose. The hot metal is allowed to flow from the reaction crucible into the mold, where the ends being joined are fused by the great heat, and upon cooling, the mass solidifies as a whole. This process is applicable to wrought iron, steel, cast iron, and other metals whose oxides are capable of reduction by aluminum, as for example, nickel, manganese, and chromium.

Many metallic sulfides also react with aluminum powder; aluminum sulfide and the other metal in the free state are formed. Hence, the Thermit process is much used in obtaining metals from sulfide, as well as oxide ores.

Copper

Sources.—Copper is one of the most widely distributed of metals. It is mined in nearly every country in Europe, in Siberia, Japan, Chile, Mexico, Canada, Australia, and Africa, but about one-third of the world's total smelter output of copper is produced in the United States. As reported in "Minerals Yearbook, 1938,"[1] the

[1] Bureau of Mines.

states that lead in production, in order of decreasing importance, are Arizona, Utah, Montana, Nevada, and Michigan.

Ores.—Copper is one of the comparatively few metals that are found in the metallic state. Free or native copper, scattered through beds of amygdaloidal[1] and conglomerate rocks, is found in the upper peninsula of Michigan. The copper content of the rock is about 1 per cent. The metal is itself very pure, averaging above 99.9 per cent copper. The impurities consist of traces of arsenic, silver, iron, and nickel. Native copper from this source is known as "Lake" copper. According to the statistics of the U.S. Bureau of Mines it now constitutes only about 5 per cent of the domestic output.

Other copper ores belong to that which is known as the oxide group. This group includes not only the oxides proper, but other compounds containing them, such as the hydroxides, carbonates, silicates, and sulfates. Important members of this class are *cuprite* or *ruby copper*, Cu_2O; *melaconite*, CuO; *azurite*, the blue carbonate, $Cu(OH)_2 \cdot 2CuCO_3$; *malachite*, the green carbonate, $Cu(OH)_2 \cdot CuCO_3$, a great deal of which was formerly found in Arizona; and *chrysocolla*, $CuSiO_3 \cdot 2H_2O$.

About 70 per cent of the copper produced in the United States is obtained from sulfide ores. In Montana and Utah are found large deposits of this character. Important members of the sulfide group are *chalcocite* or *copper glance*, Cu_2S; *covellite*, CuS; *chalcopyrite*, $Cu_2S \cdot Fe_2S_3$; *bornite*, $3Cu_2S \cdot Fe_2S_3$; and *tetrahedrite*, $4RS \cdot (Sb, As)_2S_3$, in which R may be Cu, Fe, Zn, or Ag_2, and which may contain 15 to 48 per cent of copper. The chalcocite and chalcopyrite have been the most important economically.

Reduction of Ores.—With but few exceptions, one of which has just been noted, the metallic content in copper ores is not high; it rarely exceeds 10 or 15 per cent, and not infrequently is as low as 2 or 3 per cent. On this account it is usually necessary to work over a large amount of earthy material. Smelting methods vary, of course, with the kind of ore, *i.e.*, whether it is native copper, or belongs to the oxide or sulfide group.

With native copper the smelting process is not difficult. The metal is first concentrated by crushing, grinding, and washing the ore. The remaining gangue, rocky or earthy matter, is then removed by heating the concentrate in a furnace in the presence of a suitable flux, usually limestone. The copper melts and collects

[1] Almond-shaped or elliptically globular, generally of lava origin.

beneath the silicate slag that is formed by the reaction between the flux and gangue. The melted metal is poured from the furnace and cast in ingots.

The oxide ores when rich in copper were formerly smelted with coke or charcoal and a suitable flux in blast furnaces similar to those employed in the iron industry (page 264) except that the sides were jacketed with running water to keep them cool. This practice is still continued in some localities for screened ore with lumps averaging 2 in. in diameter, but now, because modern methods of concentration yield a very fine product, the blast furnace is little used. A fine concentrate cannot be worked satisfactorily in the blast furnace.

Owing to the great success of flotation (described later) as a method of concentrating sulfide ores, there is at present, in handling oxide ores, a tendency to mix them with sulfide ores and then proceed with the regular sulfide process of reduction. Although the sulfide smelting process involves many more operations, the advantages of the sulfide concentrating process more than offset any objections that may be offered against later steps in the procedure.

Of the three classes of copper ores, the sulfide group is, indeed, the most difficult to smelt. The process is complicated because, in addition to the sulfur, it is necessary to remove the large quantity of iron which these ores carry. In most cases small quantities of lead, arsenic, antimony, or other elements are present, and these metals also must be eliminated. Since approximately three-fourths of the copper derived from domestic sources comes from sulfide ores, the process by which the metal is obtained from them will be discussed more fully than has been done for the preceding groups.

Because the ores differ so greatly in composition and physical character, the smelting process differs in different localities. In general, however, the several steps are as follows: (1) concentrating, (2) roasting, (3) smelting, (4) converting, and (5) refining.

1. Concentrating.—Concentration is not required in all cases; it is necessary only with low-grade ores. The older methods of concentrating ores, consisting chiefly of crushing, grinding, and washing, or levigating with water, often left as much as 30 per cent of the copper in the rejected tailings. Comparatively recently, however, a new process, known as *flotation*,[1] has been developed in which 95 per cent of the copper is saved, and two-thirds of the ore is

[1] GAUDIN, "Flotation," McGraw-Hill Book Company, Inc., New York (1932).

discarded. With 3 per cent of copper in the original ore, there will be at least 8 per cent in the concentrated product. The new process has even made it profitable to rework the rejected dumps of earlier operations. Because of its great economic value, flotation is without doubt the most important recent development of modern nonferrous metallurgy.

The operation of the flotation process involves a peculiar phenomenon. In the liquid in which the ore is treated, the heavier mineral particles are made to rise, while the lighter rock particles, or gangue, sink. For the purposes of study, the process may be divided into three steps.

a. Oiling.—The ore, which has been ground to an impalpable fineness, is worked into a pulp or slime with water in the presence of less than 1 per cent of coal tar and creosote. Too much of this mixture must not be used, or, due to the formation of oil films of appreciable thickness, an effect entirely different from that desired will be produced. When the proper small quantity of the tar-creosote mixture is used, some change is effected on the surfaces of the metallic or sulfide particles of the ore which makes them less easily wetted by the aqueous part of the mixture. The gangue appears not to be affected by the oily reagent and is consequently wetted by the water. The selective wetting effect of the water on the gangue may be increased by the use of acids, alkalies, mercaptans, and other reagents.

b. Frothing.—The ore ground with the oily reagent and water is now introduced into a larger volume of water containing a frothing reagent and the whole mass is beaten or blown so that a froth or foam is produced. In practice the flotation process differs in many particulars. At this point, for example, in some cases the oiling reagent acts as the froth producer and in other cases it is necessary to add a "frother" such as pine oil. The required procedure is determined by experimenting with the individual ores. When the froth is formed, the oiled mineral particles adhere to the bubbles very tenaciously, and are buoyed up by them. The waste silicate matter, or gangue, settles out.

c. Skimming and Recovery.—By removing the froth from the surface of the liquid, the metalliferous portion of the ore is recovered. The froth must, of course, be of sufficient permanence to last until it can be removed, but it should then quickly die away. When the froth has subsided, the slime that remains is dewatered in some kind of thickening or filtering device. The oil is distilled and used again.

The flotation process has made it possible to smelt ores that could not be worked economically by older methods. It is claimed that the process will remove 95 per cent of the copper from an ore containing as little as 2 per cent of the metal.

2. Roasting.—The ore, concentrated or not as required, is roasted to expel the volatile oxides of arsenic and antimony as much as possible, and to oxidize about three-fourths of the sulfur present. At this stage the removal of all of the sulfur is not desired. In the roasting furnace, the charge, heated to redness but not fused, is stirred constantly, and a plentiful supply of air is admitted. After the oxidation is well started, it continues of itself without additional fuel; the heat necessary to keep the process going comes from the burning of the sulfur itself. By roasting, the sulfur content of the ore is reduced from about 33 per cent to about 8 per cent, and a part of the copper and iron sulfides is changed into oxides.

3. Smelting.—While still hot, the product of the roasting furnace is conveyed into a reverberatory furnace[1] to be smelted. In some instances, especially with coarser ores, the smelting may be carried out in a blast furnace. With the increase in the use of flotation as a method of concentrating the ore, which process yields a fine concentrate, the reverberatory furnace is gradually replacing the blast furnace in copper metallurgy. As far as the lining is concerned, the reverberatory furnace employed here is not unlike the basic open-hearth steel furnace (page 288); the roof and sides are lined with silica brick and the bottom, or hearth, with magnesite or silica. The fuel employed may be oil or powdered coal. The air blast used in "atomizing" the oil or in blowing in the powdered coal, together with additional draft, is sufficient to produce a flame that is at least slightly oxidizing in character.

To the charge of roasted concentrate, known in the works as "calcine," silica (sand) is added, unless a sufficient quantity is initially present in the concentrate, in order that it may combine with the iron oxide, FeO, to form a slag. Lime, also, is generally added to form a calcium silicate that makes the slag more fusible and less sluggish. Through the medium of the slag, much of the iron in the form of iron silicate is separated from the copper.

Any iron pyrite, FeS_2, remaining in the charge is converted into ferrous sulfide, FeS, by distilling off the excess sulfur. A small amount of sulfur is burned to sulfur dioxide and part of the ferrous

[1] For description and illustration of a reverberatory furnace see pp. 276 and 388.

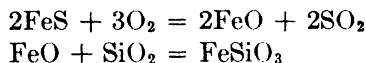
sulfide is converted into ferrous oxide, which in turn enters the slag as previously stated.

With the remaining ferrous sulfide, FeS, the cuprous sulfide, Cu_2S, forms a heavy, melted mixture, which, because its specific gravity is about twice that of the slag, collects beneath the slag. This sulfide mixture is known as *matte*. Besides the sulfides of iron and copper, the matte contains a considerable amount of metallic copper, a little metallic iron, and any gold, silver, or other heavy metals that were present in the ore.

4. Converting.—In this stage of the process the matte is changed to metallic copper by blowing air through the melted mass while it is contained in a receptacle known as a converter. In principle, the converter employed is similar to the bessemer converter (pages 279 and 281) used in the steel industry, except that it is as a rule wider and shallower with a greater capacity than the steel bessemer, and that the air is introduced low on the sides, rather than in the very bottom. The copper converter, however, unlike the steel converter employed in American practice, is basic-lined; the lining consists of magnesia brick.

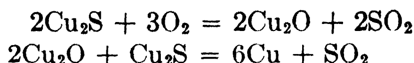
A charge of melted matte is conveyed into the converter, a little sand or raw ore is added, and air under a pressure of about 15 psi is blown through the liquid mass. The sulfur burns to sulfur dioxide, and the ferrous sulfide is converted into ferrous oxide. As the ferrous oxide forms, it reacts with silica of the sand or with the silica and the alumina of the raw ore to form a slag. When the iron has been slagged from the matte, the blast is stopped and the slag is poured off. The blowing is then resumed. Now the copper sulfide is oxidized. The copper oxide formed reacts with unchanged sulfide to yield metallic copper. The chief reactions occurring in the converter may be summed up as follows:

First stage



$$2FeS + 3O_2 = 2FeO + 2SO_2$$
$$FeO + SiO_2 = FeSiO_3$$

Second stage



$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

Approximately 5 hr. are required to complete these reactions as compared to the 15 min. required for the conversion of pig iron into steel (page 283). The yield of copper is about 99 per cent pure. It

is called "blister copper" because, when cast, sulfur dioxide which was dissolved in the melted metal separates in the form of bubbles. On the surface of the solidified metal the bubbles appear as blisters.

Refining.—Because of the detrimental effect of even very small quantities of impurities on the electrical conductivity[1] of copper, the electrical industry, which consumes over half the copper produced in the United States, demands a purity of at least 99.95 per cent. To meet this requirement, the copper is subjected to a refining process.

There are two ways of refining copper: fire refining and electrolytic refining. It is only by the latter process, however, that metal sufficiently pure for the electrical industry can be produced.

In fire refining, which is the older method. the converter metal is transferred to an acid-lined furnace with a basin-shaped hearth. At first, the flame is kept strongly oxidizing in character. As soon as the sulfur has been removed, oxidation is carried on by means of air jets aided by some method of mechanically agitating the melt to expose more surface. Cuprous oxide is formed, which in turn acts as an oxidizing agent for the baser metals. Their oxides then escape as a fume, or are slagged by combining with the silica of the lining. An excess of cuprous oxide is left, and must be reduced, since if allowed to remain, it causes the metal to be in a condition known as "dry," which means that it is brittle, breaking with a granular fracture, instead of being tough with a fibrous fracture. Reduction is accomplished by covering the molten charge with charcoal or coke and stirring with a pole of green wood. The wood undergoes destructive distillation, and the gases that escape, in addition to having a reducing effect, bring about a violent bubbling and stirring of the melted metal, which allows occluded oxidized bodies to rise. Overreduction must be avoided, since the copper almost always contains traces of the oxides of arsenic, antimony, and bismuth which in their oxide state are not so objectionable; but if the reducing action of the carbon and the gases from the pole is too great, these oxides are reduced, and the resultant metals are more active in producing brittleness than the cuprous oxide itself.

Even in the electrolytic method, the metal is given a preliminary fire refining to remove as much as possible of the impurities and to secure as nearly as possible a uniform product. It is then cast in the form of slabs about 3 ft. square and 2 in. thick weighing approximately 500 lb., which are known as anode plates. It is cheaper

[1] See Physical Properties, p. 125.

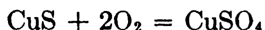
to remove the major impurities by the furnacing process than by electrolysis, and, in addition, if the anodes are of uniform composition much better results can be secured in the electrolyzing bath.

In electrolytic refining there are two methods of connecting the electrodes: multiple and series. In the former, the anodes, connected in multiple, are suspended between similarly connected thin sheets of pure copper in a warmed, constantly circulated bath of copper sulfate solution acidified with sulfuric acid. An electric current of relatively low voltage and high current strength is employed; the current density is about 25 amp. per sq. ft. of cathode surface. As the current passes through the system, copper at the anode surface is oxidized and passes into solution as copper ions. At the cathode surface, copper ions are discharged and adhere there as metallic copper. Thus, the anode gradually dissolves away and the cathode builds up. By suitably regulating the potential drop across the cell, it is possible to avoid dissolving a great many of the impurities contained in the copper. These impurities, together with bits of copper, drop from the anode and collect as an anode slime. The chief components of the slime are copper, silver, gold, platinum, salts of bismuth and antimony, cuprous oxide, lead sulfate, silver chloride, sulfur, selenium, and tellurium. The gold, silver, and platinum recovered from the slime constitute a noteworthy source of profit. Although metals such as iron, zinc, and nickel dissolve at the anode, the tendency of their ions to discharge at the cathode is less than the discharge tendency of the copper ions; consequently, under the operating conditions they are not plated out. By this method, cathode copper having a purity of approximately 99.955 per cent is obtained. Because the cathode plates are somewhat granular in texture and do not stand shipment well, small pieces being broken off, the copper is not marketed in this form, but is melted and cast in bars. The melting lessens the purity slightly.

In the series system there are no starting sheets; the back of each anode serves as the cathode for the preceding anode. These anodes, which may be either rolled or cast, are thin; the thick heavy slabs employed in the multiple system do not serve satisfactorily here.

Leaching.—The copper from low-grade oxidized ores and from old tailings may be extracted by a suitable reagent. From old tailings the metal may be obtained by leaching directly, whereas more recent tailings must be oxidized by roasting prior to leaching. By long continued exposure to the weather, a wet oxidation

occurs which yields a soluble product. The action may be illustrated as follows:



$$CuS + 2O_2 = CuSO_4$$

This reaction occurs in mines; as a result, some mine waters contain enough dissolved copper salts to render recovery profitable.

Ores and tailings are extracted in vats with acid-proof linings and filter bottoms. The solvents used may be sulfuric or hydrochloric acids, aqueous solutions of iron salts, ammonia water, ammonium-carbonate solution, or similar reagents. From the solution the copper is recovered either by electrolysis or by precipitation with metallic iron.

Recovery of Dust and Fume.—In the several furnace operations in copper smelting, a great deal of dust is produced. The amount of the dust has been increased in recent years by the fineness of the concentrate supplied by the flotation process. Dust recovery is an important item of plant economy. For the most part, the flues of all the furnaces in a copper-smelting plant lead to a single mammoth stack. The point of entry to the stack then constitutes a convenient place for dust recovery.

One of the simplest methods is to establish at the base of the stack large dust chambers through which the gases pass at low velocity. In a modification of this system, wire baffles on which the dust impinges and adheres are placed in the dust chambers. While the gas stream is being diverted through another chamber, the dust is dislodged from the baffles and recovered.

For extremely fine particles, such as fumes, electrostatic precipitation, of which the Cottrell system is a well-known example, is serviceable. In one of the Cottrell installations, corrugated-steel roofing sheets, spaced 12 in. apart, with rows of small chains between them, are hung in boxlike chambers. The chains are electrified with a static charge under very high tension. As the dust passes into the electric field surrounding the chains, the particles become charged and are repelled from the chains to the plates. The plates being grounded, the dust particles discharge there and collect in masses large enough to fall through the rising stream of gases.

Physical and Mechanical Properties.—Copper is the only reddish-colored metal. It is second only to silver in electrical conductivity, and of the half million or more tons produced in this country annually about one-third is used in the electrical industries. Although pure copper is one of the best conductors of heat and

electricity, its electrical conductivity is highly sensitive to the presence of impurities. The following percentages will serve to illustrate their effect: as little as 0.03 per cent of arsenic will lower the electrical conductivity about 14 per cent; 0.13 per cent of phosphorus will lower it 30 per cent; and 0.4 per cent of iron, 64 per cent.

If copper is heated to a red heat and cooled slowly, it becomes brittle; but if cooled quickly it is soft, malleable, and ductile. The brittleness is due to the coarsely crystalline structure that develops during slow cooling. At red heat, copper can be welded.

Like aluminum, pure copper does not cast well. When molten it absorbs gases, such as carbon monoxide, hydrogen, and sulfur dioxide, which separate out on cooling and cause "blowholes." To produce sound castings having a high electrical conductivity, Weintraub[1] adds about 1 per cent by weight of boron suboxide to the molten copper, which has been heated to about 1350°C. To secure high conductivity, pure copper must be used, since the suboxide acts only as a deoxidizer. Sound castings can be made by this treatment regardless of the purity, but the conductivity is reduced in proportion to the amount and kind of impurity present. Although electrical conductivity as high as 97 per cent of the maximum has been obtained in castings made in this way, it is usually about 88 to 90 per cent.

TABLE 25.—PHYSICAL AND MECHANICAL PROPERTIES OF COPPER

Melting point	1084°C. (1983°F.)
Boiling point	2595°C. (4703°F.)
Density	8.94 g. per cc. (20°C.)
Electrical resistivity	1.682 microhm per cm.
Thermal conductivity	0.923 c.g.s.
Tensile strength	31,800 psi, commercial, rolled and annealed
	60,000 psi, hard drawn
Modulus of elasticity	16×10^6 psi

The ultimate tensile strength of copper varies greatly with the mechanical treatment to which it has been subjected. For cast copper, the tensile strength is about 25,000 psi; when cold rolled or cold drawn (so-called hard drawn, *e.g.*, trolley wire), its tensile strength will range from 40,000 to 67,000 psi.

For copper that is to be worked, lead is sometimes added in order that the metal may be worked more easily, but if more than about 0.5 per cent is employed, it causes the copper to be brittle. In copper alloys for casting, as much as 10 to 20 per cent may be

[1] *Gen. Elec. Rev.*, **15**, 459 (1912).

added to cheapen the product, but this lead largely separates out in globular masses on cooling. At the melting point of lead, copper is practically insoluble in liquid lead, and less than 0.05 per cent of lead enters into solid solution (page 214) in the copper.

The physical and mechanical properties of copper are summarized in Table 25.

Chemical Properties.—When exposed to dry air, copper slowly turns dull, due to the formation of a thin film of the cuprous oxide. In moist air, it becomes coated with a green basic carbonate, $Cu(OH)_2 \cdot CuCO_3$, incorrectly called verdigris, which is closely adherent and protective. In the presence of atmospheric hydrogen sulfide, it is rapidly darkened by the formation of cupric sulfide, but the film is protective. On the whole, copper is quite permanent under the usual conditions of outdoor exposure.

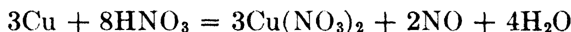
When heated in the air, it becomes coated with a layer of the black cupric oxide, CuO, beneath which will be found a layer of the red, cuprous oxide, Cu_2O.

Although copper does not dissolve in hydrochloric and dilute sulfuric acids with the evolution of hydrogen, both these acids attack the metal slowly in the presence of oxygen. It is soluble in hot concentrated sulfuric acid, with the evolution of sulfur dioxide:



$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

It is readily soluble in dilute or concentrated nitric acid:



$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

It is important to remember that many organic acids, even when dilute, act upon copper. Such acids are often found in food products and may come into contact with copper used in making utensils for cooking. All copper compounds are poisonous.

Ammonia water slowly dissolves copper in the presence of air with formation of a complex ammine, $Cu(NH_3)_4(OH)_2$; a blue-colored solution is produced.

Uses of Copper.—The largest proportion of copper produced is employed for electrical purposes. About one-fourth is consumed in making brasses, bronzes, and other copper alloys. It is used for sheeting, roofing, spouts, boilers, stills, and condensers, and other purposes where corrosion resistance with fair strength and flexibility is essential.

Lead

Occurrence.—Lead is a very widely distributed metal; it is found in nearly every country of the world. About 70 per cent of the total output of all countries, however, is produced by five of them, the United States, Australia, Mexico, Canada, and Germany. Other large producers are Belgium and India. Russia and China have immense deposits of ore, but their output is small because they are not extensively worked. In the United States the leading states in order are Missouri, Utah, Idaho, and Oklahoma.

The production of lead in the United States has been gradually increasing for many years, but this has not been due to any recent discovery of new ore bodies. There are probably within the United States no deposits of any consequence that remain to be discovered, and the fields now being worked are slowly being exhausted. The increase in output has been due to better methods of ore dressing, especially to selective flotation. By this method it has been possible to derive lead from complex ores that were formerly considered to contain so little lead that it could not profitably be recovered. In the last few years the rate of increase in the output of Canadian lead has been greater than that of any other country. The most of it is produced in British Columbia. It is interesting to note that Spain's lead deposits, which are still important, are the same deposits that were worked by the Romans in the third century B.C.

It seems now that Africa will make a considerable contribution to the world's future supply of lead. Important ore fields have been found in Morocco, Rhodesia, and in the South-West Africa mandate.

Ores.—In deposits of their ores, lead and zinc are generally associated. The mixtures, of course, vary greatly in proportions. In one locality it will be lead and in another zinc that predominates, but neither metal is likely to be found entirely free from the other. Not infrequently lead mines become zinc mines at lower levels. Zinc minerals weather more readily than those of lead and are often carried by water to lower levels more rapidly and completely than lead.

Lead sulfide, PbS, called *galena* or *galenite,* is the chief lead ore. Its distribution is very wide. There are practically no important deposits of lead in which galena is not present to some extent. Silver sulfide is scarcely ever absent from galena; the amount is small, however, generally being less than 0.3 per cent.

Second in importance as an ore of lead is *cerussite*, the carbonate, $PbCO_3$, immense deposits of which are found in Colorado and Nevada. Prior to the discovery of these deposits, cerussite was considered to be of little value. During the 16 years that followed the gold strike in 1860 on the present site of the city of Leadville at the upper end of the Arkansas River valley in Colorado, the placer miners thoughtlessly moved aside the great boulders and "heavy sands" that obstructed their work, unaware that they were part of a deposit of lead ore, extremely rich in silver, worth more by many hundreds of millions of dollars than all of the gold that would ever be removed from that district. Cerussite is a secondary formation; it has been formed by the weathering of galena. In some mines cerussite is found near the surface and galena at lower levels.

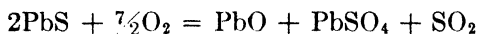
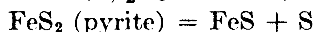
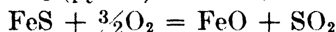
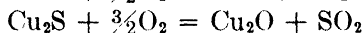
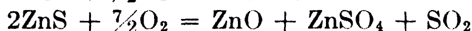
Anglesite, $PbSO_4$, and *pyromorphite*, $3Pb_3P_2O_8 \cdot PbCl_2$, are lead ores of minor importance. Other lead minerals also are found.

Metallurgy of Lead.—If the metallurgy of lead involved no more than the extraction of lead from galena or from cerussite, the process would be extremely simple. In practice, however, the process is not simple because lead ores are very complex. In addition to the zinc and silver, of which mention has already been made, in lead ores, antimony, arsenic, bismuth, cadmium, manganese, iron, nickel, cobalt, copper, gold, and other metals may be present. The process must be adapted to the recovery of some of these elements because they are valuable; others must be removed from the lead because they affect its properties adversely.

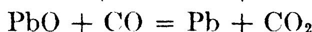
Flotation.—In accordance with modern practice in handling ores, the sulfide ores especially, if concentration of lead ores is required it is generally done by flotation (page 141). It has been found that the intimate mixtures of sulfides in lead ores may be not only parted from the gangue, but may themselves be separated by a process of selective flotation. If the flotation liquid is made faintly alkaline with soda ash, and a little sodium cyanide and zinc sulfate are added, zinc sulfide and iron pyrite may be floated without bringing up the sulfides of copper and lead. In a second treatment, by making the liquid more alkaline, the zinc sulfide is floated from the iron pyrites. The copper is removed from the lead later during refining.

Blast-furnace Smelting.—Today practically all lead smelting in this country is carried out in the blast furnace. The principal ore of lead, galena, PbS, contains also sulfides of Zn, Fe, Cu, Sb, and As, and silicates and carbonates of Ca, Fe, Al, Mg, etc. Small amounts

of Au and Ag are likewise present. The ore is first subjected to a roasting process at temperatures between 450 and 700°C. with free access of air. A considerable amount of sulfur is removed and other important chemical changes occur. Some typical reactions are


$$2PbS + 7/2O_2 = PbO + PbSO_4 + SO_2$$

$$FeS_2 \text{ (pyrite)} = FeS + S$$

$$FeS + 3/2O_2 = FeO + SO_2$$

$$Cu_2S + 3/2O_2 = Cu_2O + SO_2$$

$$2ZnS + 7/2O_2 = ZnO + ZnSO_4 + SO_2$$

This roasted material is mixed with coke, fluxes, and some scrap iron and is introduced into a water-cooled blast furnace. This furnace is quite similar to that used in the recovery of copper, except that the temperature of operation is much lower. The essential reduction reactions are

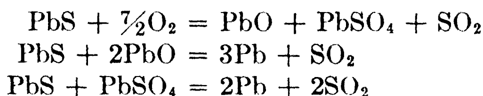

$$PbO + C = Pb + CO$$

$$PbO + CO = Pb + CO_2$$

$$PbS + Fe = Pb + FeS$$

The molten lead collects in the crucible at the bottom of the furnace, from which it is tapped at intervals. Above the lead a matte of copper and iron sulfide, containing some lead, collects and above this a slag consisting principally of silicates of Fe and Ca. This likewise is tapped off and then the matte is separated from the slag. A retreatment of the matte in a blast furnace removes most of the lead and results in a final matte of sufficient copper content to be treated for the recovery of this metal.

Reverberatory or Ore-hearth Smelting.—This is the oldest method of treating lead ores, but it has practically passed out of use in this country. It is applicable only to ores of high purity, containing at least 55 per cent of lead and less than 5 per cent of silica. The labor costs on the earlier hand-rabbled ore hearth were excessive, and even with the introduction of mechanically raked hearths this method cannot compete with the high-capacity blast-furnace process. Briefly, the furnace consists of a cast-iron well or hearth box set in brickwork and supplied with tuyères for the admission of an air blast and with necessary hood and flues. The ore is mixed with small amounts of lime and covered with a little coke. A blast of air is admitted for three or four minutes, and the combustion of the coke raises the temperature of the mass sufficiently to fuse it partly. This is drawn out on the work stone in

front of the furnace where the slag is separated. The molten lead trickles down into a receptacle and the unreduced ore is returned to the furnace. Lead also collects in the furnace well and overflows through spouts. The important chemical changes involved in the reduction of the ore are illustrated by the following reactions:



$$PbS + \tfrac{7}{2}O_2 = PbO + PbSO_4 + SO_2$$
$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

Leaching.—An increasing tonnage of lead is being extracted from ores by a method of brine leaching. Galena ore, roasted to sulfate, is leached with a chlorinated solution of sulfuric acid saturated with sodium chloride. In some cases, raw ores are leached. The lead is recovered from the leach liquor by electrolytic deposition with high current density. The sponge lead that collects on the cathode is removed and pressed into cakes for melting.

Refining of Lead.—The lead obtained from practically all ores, except those found in the Mississippi valley and in parts of Germany and Spain, contains enough silver to pay for its extraction. This argentiferous lead, called base bullion, is likely to contain also other precious metals such as gold, platinum, and palladium. In refining the lead, not only must these metals be recovered, but the impurities, such as sulfur, arsenic, antimony, bismuth, tin, copper, iron, nickel, and cobalt, all of which are very detrimental in their effect on the lead, must be removed, and for the most part must be worked up into salable products.

Softening.—The base metal impurities make the lead hard and unfitted for most of its uses. The treatment employed for their removal, therefore, is spoken of as a softening process. Nearly all of these impurities fortunately combine with oxygen more readily than lead, and can be taken out by an oxidizing treatment. As their oxides are formed, they collect on the surface as a dross, which is removed by skimming. Copper and bismuth cannot be effectually eliminated in this manner. Copper, however, forms an alloy with lead that is less fusible than the lead itself. By suitably regulating the temperature of the melt, use may be made of this fact to effect its removal. Bismuth is generally separated subsequently in connection with the process of desilvering.

Desilvering.—The softened lead still contains the silver and other precious metals. There are three principal methods employed for their removal: the Pattinson, the Parkes, and the Betts.

1. The Pattinson process: This method is based upon the fact that when argentiferous lead is cooled to its solidification range, the lead crystallizes selectively, rejecting the silver which remains in the melt. The crystals of lead are skimmed out, more silver-bearing lead is added, and the process is repeated. When the silver content of the liquid lead reaches about 500 oz. per ton, it is removed from the pot and cupeled. In cupellation the metal is subjected to an oxidizing process. The lead is converted into litharge, PbO, while the silver is practically unaffected by the oxidizing attack. Gold and other metals remain with the silver.

2. The Parkes process: This method of desilvering lead is based on the fact that at temperatures near the melting point of zinc, liquid zinc and lead are practically immiscible, like oil and water. Two layers form with the less dense zinc floating on the lead. Very little lead is present in the zinc layer and relatively little zinc dissolves in the lead. Furthermore silver (and gold) distribute themselves between these layers so that the zinc layer contains most of the precious metal originally present in the lead. If the temperature is lowered somewhat, the zinc-silver (gold) alloy solidifies and can be skimmed off. The zinc is first brought into intimate contact with the lead by stirring, then is allowed to rise, and the crust that it forms is removed. Two or more treatments with zinc are required. The zinc is recovered from the crust by distillation and is employed again. The relatively small amount of lead remaining with the silver is removed by cupellation.

Whether the Pattinson or the Parkes method is employed depends partly upon the bismuth in the softened lead. In the Pattinson process the bismuth stays in the silver-bearing lead and is removed by cupellation; in the Parkes process the bismuth remains in the desilvered lead that goes to market. High-bismuth lead, therefore, is more successfully handled by the Pattinson process. On the other hand, because the Parkes method is cheaper to operate, allows less silver to remain in the lead that is marketed, and recovers completely even traces of gold, it is the desilvering process most generally used in the United States.

3. The Betts process: Some lead, especially that with a high-bismuth content, is refined by electrolysis. The scheme is very similar to that employed in the electrolytic refining of copper (page 145). The electrolyte is a solution of lead fluosilicate, $PbSiF_6$. Gold, silver, and bismuth remain unattacked at the anode, and are recovered from the anode slime. Although ordinarily the

lead deposit on the cathode is spongy, if a little gelatin or some similar colloidal substance be added to the fluosilicate electrolyte, a solid cathode deposit as dense as cast lead is secured. As little as 1 part of gelatine to 5,000 parts of solution is required to produce this effect.

Commercial Lead.—In commercial lead from different sources there may be a marked variation in the amount of impurities carried. The refining that nonargentiferous[1] lead receives is sometimes scanty. It may be no more than a slow melting down and stirring with a pole of green wood or with dry steam to allow entangled slag and other oxide inclusions to rise. Some purification through oxidation, of course, will occur in this process. Lead containing over 0.05 per cent of bismuth cannot be used for "corroding" lead in the manufacture of white lead (page 550) because bismuth imparts to the white lead a grayish color. A good quality of corroding lead will contain from 99.95 to 99.99 per cent of lead. All the usual impurities, arsenic, antimony, bismuth, zinc, and copper, increase the hardness of lead. Zinc also lessens both its resistance to acid attack and its suitability for the manufacture of lead-tin solder.

Properties.—Lead is a bluish-gray metal with a high metallic luster when freshly cut. It is the softest and heaviest of all the common metals. It can readily be scratched with the fingernail when pure, and is the least tenacious of the common metals. It is very malleable and may be readily formed into foil. When hot it may be extruded by hydraulic presses into tubes, rods, and wire. Under a pressure of 29,000 psi, filings and shearings can be pressed into a solid block. Under a pressure of 75,000 psi, it appears to liquefy at ordinary temperatures. The properties of lead are summarized in Table 26.

TABLE 26.—PROPERTIES OF LEAD

Melting point	327.4°C. (621.3°F.)
Boiling point	1744°C. (3169°F.)
Density	11.35 g. per cc. at 20°C.
Electrical resistivity	20.65 microhms
Thermal conductivity	0.083 c.g.s.
Tensile strength	1,600 psi, very pure 2,000 psi, ordinary
Modulus of elasticity	2.56×10^6 psi
Hardness	4.1 Brinell

[1] Containing no silver.

Chemical Properties.—Lead is not affected by perfectly dry air or by water that is free from air. In the presence of both air and moisture, clean lead surfaces rapidly acquire a thin film of the basic carbonate. The film adheres closely and retards further action. Under severely corrosive conditions, as when buried in cinders, lead is rapidly attacked. In this location, a white incrustation of the carbonate, sulfite, and sulfate is produced.

Lead is quickly tarnished by atmospheric hydrogen sulfide; a layer of black lead sulfide is formed. In normally dry air the sulfide layer is protective but, if exposed to the weather, the sulfide is oxidized to the sulfate which forms a whitish efflorescence.

If melted in contact with air, a dark scum or coating of the suboxide, Pb_2O, appears. If the temperature is raised to a dull-red heat the suboxide is converted into the monoxide, PbO. This oxide finds wide application in the arts, especially in paints as a drier. It is manufactured by heating lead in air, and removing the film of oxide as it forms. If produced at a temperature below the melting point of the oxide, the product, which is an extremely fine powder, is called *massicot*. When formed at a temperature above its melting point, the oxide, which solidifies as a stonelike mass, is known as *litharge*. On standing, the massive litharge crumbles into orange-yellow scales called *flake litharge*, which must be ground to a powder for use. If the litharge is heated in air to a temperature between 400 and 450°C., it is converted into *red lead* or *minium*, Pb_3O_4.

Lead is resistant to the action of the alkalies, such as caustic soda and potash. It is not much affected by cold hydrochloric or sulfuric acid; it is especially indifferent to the latter. The lead salts of these acids are insoluble in the cold, so that some protection is afforded the metal after the acid has attacked the surface slightly. Lead is quite soluble in nitric acid, and in the presence of air is noticeably attacked by acetic. Many of the relatively weak organic acids, such as are found in food products, dissolve lead slightly, so that lead should not be allowed to remain in contact with foods or beverages. All lead salts are poisonous. According to the manner in which they act, they belong to the accumulative class, *i.e.*, small amounts taken daily seem to be stored within the system until a toxic quantity is present. Absorbed lead may remain in the body for years. Very pure water dissolves lead sufficiently to make it dangerous for continuous use. When the lead is in contact with hard water, an insoluble coating of lead carbonate and sulfate is formed on the metal; this coating prevents the water from being

contaminated. With pure water, such as rain water, lead hydroxide, which is noticeably soluble, is formed. Consequently, lead pipes are suitable for conveying drinking water only when the water is hard. At the present time, however, lead pipes are used chiefly for waste lines. Stains and splashes of paints containing lead pigments should not be allowed to remain upon the skin, because lead compounds from this source are absorbed through the skin.

Uses of Lead.—From the time of the Romans, at least, lead has been used for the making of tubes or pipes; in fact, from the Latin word for lead, *plumbum*, has been derived the name "plumber." Lead is employed for chemical laboratory and plant drains, and for chemicalproof plumbing in general. It finds extensive application as sheaths for electric cables, both overhead and underground. In the form of sheet lead it serves excellently for roofs, gutters, and cornices. Large quantities of the metal are consumed in the manufacture of the lead sulfuric acid-type of storage battery, and in the manufacture of white lead and other paint pigments.

As given by "Minerals Yearbook, 1937," the percentages of the total lead consumed in the United States for major uses were as follows:

Use	Per Cent
Storage batteries	28
White lead, red lead, litharge	21
Cable coverings	13.5
Building	6.6
Ammunition	5.8
Solder	3.2
Foil	3.2
Type metal	2.5
Bearing metals	2.2
Calking	2.2

The uses indicated account for more than 88 per cent of the total consumption.

In addition to the solder and bearing alloys, mentioned in the accompanying table and discussed on pages 248 to 252, lead enters into a great variety of other alloys, such as brasses and bronzes, pewter, low-melting-point alloys for sprinkler heads, safety plugs in boilers, fire-door releases, and fuses.

Tin

Occurrence.—There is only one tin ore of any importance, the stannic oxide, SnO_2, called *cassiterite* or *tin stone*. In Cornwall and Devon, in the south of England, it has been found in comparatively

large quantities. As early as 1000 B.C. these deposits were worked by the Phoenicians, and for many centuries in more modern times they were the best-known source of tin, but now the mines are almost exhausted. At present the chief producers of tin, in order of importance, are the Federated Malay States, the Dutch East Indies, and Bolivia. Approximately two-thirds of the world's total production of 210,000 tons of the metal comes from these three sources. Nearly the total output of the Dutch East Indies is supplied by the islands of Banca and Billiton, lying between Sumatra and Borneo. In the tin trade the terms "Straits tin," for Malayan tin, and "Banca tin" have long been common.

Other countries producing small amounts of tin are Thailand, Nigeria, China, and Australia. Tin is the one metal of major industrial importance that is not found in considerable quantity in the entire North American continent. We import into the United States about 80,000 tons per year, valued at better than $104,000,000.

Mining and Metallurgy of Tin. *General Considerations.*—Cassiterite, the tin ore, is found in two types of deposits: (1) in primary deposits in the form of veins or lodes; and (2) in transported alluvial (water-borne) or placer deposits. The transported deposits, of course, had their origin in the weathering of the primary deposits. The latter are practically always in, or closely connected with, granite or other acid eruptive rocks. According to the type of deposit, tin ore is designated either as "vein tin" or "stream tin." Although the other minerals associated with tin oxide in the ore are decomposed by weathering, the cassiterite, being very stable, is practically unaffected. Owing to the removal of the decomposition products by the dissolving and washing action of the transporting water, the tin ore in placer deposits is much more nearly pure than that in the original vein formations. Most of the Malayan and East Indian tin is obtained from alluvial deposits chiefly by ground sluicing, hydraulic mining, and dredging; practically all the ores from Bolivia, China, and Nigeria are taken out by vein mining. This fact has an important bearing on the quality of the tin coming to the market from these sources. Tin smelted from Asiatic ores is much purer than that from Bolivian and other ores.

Because of a prohibitive export duty, all tin ores mined in Great Britain and her possessions are required to be smelted within the British Empire.[1] As a result, most of the Malayan ores are smelted

[1] HILL, *Eng. Mining J.*, 109 (1913).

at Singapore and Penang. The latter town is located on a small island just off the west coast of the peninsula. Similar restrictions operate to prevent the exporting of tin ores from the Dutch East Indies, and these ores also are smelted locally. Owing to British control, even the Bolivian ores are smelted chiefly in England. Today there is not a single tin smelter operating in the United States.[1]

Preparation of Ore.—Because the methods of refining the metallic tin after smelting are not very satisfactory, it is more essential with tin ores than it is with those of some other metals to deliver to the smelting furnace as pure a concentrate as possible. Inasmuch as the alluvial ores are originally relatively pure, mere concentration may be all that is required with such ores. This may be accomplished by washing in various types of simple sluicing devices. In this manner the lighter clay, sand, and gravel may be washed away. The same treatment may be applied to a few lode ores after crushing. Sometimes handpicking methods are used. In the more modern plants, standard wet-concentrating machinery is employed.

Some tin ores, particularly those from Bolivia, contain the sulfides and arsenical compounds of such metals as lead, antimony, bismuth, copper, and iron. Washing will not remove these minerals, but they may be removed by oil flotation (page 141).

In some cases, after washing, a further purification of the ore is effected by roasting. Much of the sulfur, arsenic, and antimony may be removed directly by volatilization in this way. After roasting, washing will remove undesirable metallic compounds that could not be removed by water from the unroasted ore. Oxides formed by roasting, such as those of copper, bismuth, and iron, may be extracted by leaching with dilute solutions of sulfuric or hydrochloric acids. Roasting with sodium chloride or sodium carbonate, followed by leaching with water, is sufficiently effective in some cases. From the several methods available, the metallurgist in charge selects that one which will yield the purest product with the ore in question.

Smelting.—Compared to the metallurgical difficulties encountered in the smelting of the ores of some metals, the extraction of tin from its ores is not difficult. Tin is found in the ore as an oxide, and the oxide is readily reduced by carbon. Either the blast

[1] At present, a tin smelter to operate on Bolivian ore is being constructed in Texas.

furnace or the reverberatory furnace may be employed. Blast-furnace smelting is much the older of the two methods.

The blast furnace employed in tin metallurgy has a rather low shaft and the blast pressure is comparatively light. The fuel may be either charcoal or coke, and the flux may be either silica or limestone as the gangue requires. The only difficulty encountered is that, if the slag is too acid, tin will be lost as a silicate of tin, and that if the slag is too basic, the tin oxide will act as an acid and will enter the slag as a calcium stannate.

If the reverberatory furnace is employed, the charge will consist of ore, crushed anthracite coal, and the necessary fluxing material. The furnace may be fired with long-flame, bituminous coal or with oil. For the smelting of fine ores and concentrates, the reverberatory is preferred to the blast furnace because the dust losses are less.

Refining of Tin.—Depending upon the amount of impurities in the concentrated ore, the reduced metal obtained by smelting will require more or less refining. For this purpose either fire refining or electrolytic deposition may be employed. The former is the older method and is the one that is the most generally used. Fire refining may involve two operations: liquating and poling. Liquating is a type of sweating process. The impure tin is cautiously heated on a sloping hearth to a temperature a little above the melting point of pure tin. The relatively pure tin then melts and drains away, and a skeleton of impure metal remains on the hearth. The hearth residue ultimately finds its way back to the smelting furnace. If the metal obtained by liquating is not sufficiently pure, it is treated by the poling (frequently called "boiling") process.

In the poling process the tin is heated to a temperature considerably above its melting point and is stirred with a pole of green wood. The steam and gases that escape produce a violent "boiling" action, which causes the metal in the bottom of the vessel to be brought to the surface. This stirring not only allows occluded nonmetallic bodies to rise but metallic impurities are oxidized as the metal comes into contact with the air. When a dross of oxides collects on the surface, it is removed by skimming. In some refineries the metal is agitated by the use of compressed air instead of the green wood.

In the electrolytic refining of tin, the method employed is similar to that used for copper and lead. A product that is more

than 99.9 per cent pure may be secured by the electrolytic method, using a fluosilicic acid bath, but even this high purity is not equal to that obtained from some of the purer concentrates derived from Banca ores.

Reclaimed Tin.—Approximately a third of the tin consumed each year in the United States consists of that which has been recovered from waste material. Not all of the reclaimed tin appears on the market in the form of the metal, however; indeed, the largest part of it is in the form of oxide, salts, and alloys. Although this is true, the recoveries are important because they release a corresponding amount of new tin for other uses.

The largest recoveries are derived from the scruff and drosses that are formed in making tin plate and terneplate (page 460). This is to be expected because the tin-plate industry is the largest single consumer of tin.

Some of the reclaimed metal comes from clean-scrap tin plate, such as the clippings left, for example, when stamping out disks for can tops and bottoms. Nearly all tin-plate scrap is detinned by one of three methods: the electrolytic alkali, the chlorine, and the alkali-saltpeter processes.

In the first process the tin coating is removed by an aqueous solution of an alkali and recovered by electrolytic deposition. The recovered metal is in the form of a spongy, granular precipitate which can be melted to pig tin.

In the second process the scrap is placed in an autoclave and the tin is removed by dry chlorine gas. The chlorine attacks the tin readily, but has practically no action on the iron. The tin is recovered as stannic chloride which is used in weighting silk, and as a mordant in dyeing it.

In the third method, by the use of a hot aqueous solution of an alkali and an oxidizing agent,[1] tin oxide is obtained which is used either for the preparation of enamels for cast iron in making sanitary ware (page 461), or is smelted to pig tin in a reverberatory furnace.

The tin coating and solder are also sweated from old tin-coated containers. The black steel sheet that remains is then melted to make sash weights. In some cases, tin from old tin-plated containers is recovered by the chlorine process. Unless the recovery can be accomplished locally, so that freight charges can be avoided, the recovery of tin from old cans is not profitable.

[1] *Met. Chem. Eng.*, (1917), p. 187.

Commercial Tin.—Because most of the tin on the market has been refined by the heat-treatment method, and because refining by this method cannot be relied upon to eliminate completely the impurities, the purity of the ore from which the tin was obtained has an important bearing upon the quality of the refined metal. This is true of all metals, of course, but it is especially true of tin. New tin, called primary tin, is generally sold under the name of the mining or smelting companies producing it, and their brands have a special significance in guiding the purchaser as to the quality of the metal. Tin ores from the Asiatic deposits are purer than those from other parts of the world, and, as a result, the metal reduced from such ores is recognized as being of superior quality. Banca tin is the purest variety; it is frequently 99.95 per cent pure. Bolivian tin and reclaimed tin, called also secondary tin, may contain from 1 to 5 per cent of impurities, chiefly lead, iron, copper, and antimony.

In one of the methods employed in gauging the purity of tin, the smelter heats the metal to a temperature a little below its melting point and then drops it from a specified height upon a stone slab. If the tin is pure, it splits into strands of granules. Tin that has been tested in this way and has been found to be pure is sold as *grain tin.* That which is somewhat less pure is known as *block tin.*

In this connection it should be remembered, as was indicated under the topic Reclaimed Tin, that the name "tin" employed in speaking of "tin cans" refers to tin plate (page 453), a product made by coating sheet iron or steel with a very thin layer of tin. Pure rolled tin is designated as *sheet tin* or *block-tin sheet.*

Properties.—Tin occurs in two allotropic modifications, known as the alpha and beta forms. Alpha tin crystallizes in the cubic and beta in the tetragonal system. The familiar malleable form is the beta modification or "white tin," which is stable from 18°C. to the melting point.

When the beta form is cooled below 18°C., it has a tendency to change to the alpha form, a gray granular powder known as "gray tin." The change is brought about very slowly, however, and the malleable form persists at ordinary low-atmospheric temperatures, although it is then in a metastable condition. The conversion into the granular form takes place most rapidly at −48°C., but it may be noticed at −15°C. Consequently, articles made of pure tin will fall to a powder if kept at low temperatures for a long time. This phenomenon was first observed when some organ pipes in Russia,

during prolonged cold weather, crumbled to dust. The transition has been found to occur in cold-storage warehouses. It is hastened by "inoculation"; that is to say, the presence of some of the transformed variety accelerates the change. Consequently, when started, it spreads rapidly. It is commonly designated as the "tin pest" or "tin disease."

It was formerly thought that another allotropic form of tin, called gamma tin, existed above 161°C., because ordinary tin heated above this temperature became brittle. At 200°C. this "brittle tin" can be reduced to powder under the hammer. It has been proved recently that extremely pure tin does not exhibit this behavior, and that the brittleness was caused by small amounts of impurities. The presence of impurities in general has a noteworthy effect on the properties of tin. Fractional percentages of arsenic, antimony, and bismuth, as well as occluded stannous oxide, lower the tenacity of the metal appreciably. Small amounts of copper and lead increase its hardness and tensile strength but decrease its malleability. Iron increases the hardness and brittleness.

We are chiefly concerned with the properties of beta or ordinary tin. It is a poor conductor of heat and electricity, as seen in Table 27. The electrical conductivity is about 12 per cent and the thermal conductivity 15 per cent that of silver. When a bar of the metal is bent, it emits a low crackling noise known as "tin cry," which is due to friction of the crystal particles moving over one another. The properties of tin are summarized in Table 27.

TABLE 27.—PROPERTIES OF TIN

Melting point	231.8°C. (449.2°F.)
Boiling point	2270°C. (4118°F.)
Density	7.30 g. per cc.
Electrical resistivity	11.5 microhms
Thermal conductivity	0.157 c.g.s.
Tensile strength	2,000 psi
Modulus of elasticity	5.9×10^6 to 7.8×10^6 psi
Hardness	5.0 Brinell (10 mm. ball, 1,000 kg.)

Chemical Properties.—Tin does not ordinarily corrode, or tarnish much when exposed to the atmosphere; in fact, it is about the most resistant of the common metals in this respect. On this account, it is much used to coat other metals. Above its melting point it oxidizes readily to stannic oxide, SnO_2. When heated to about 1550°C., it takes fire and burns with a white flame.

Tin is attacked at a moderate rate by cold, dilute hydrochloric acid; stannous chloride is formed. The action is much more rapid

if the acid is heated. Dilute sulfuric acid dissolves tin slowly with the evolution of hydrogen. Concentrated nitric acid forms stannic nitrate which is largely insoluble in the acid. If water is present, hydrolysis produces basic nitrates or orthostannic acid; however, if heat is applied, white, insoluble metastannic acid is produced.

Uses of Tin.—Although the United States produces practically no tin, it consumes more than a third of the world's total annual production. The consumption is distributed approximately as follows:

Use	Per Cent
Tin plate and terneplate*	40
Solders	22
Babbitt (p. 249)	8
Brasses and bronzes	8

* Terneplate is sheet steel coated with lead-tin alloy (p. 460).

The remaining 22 per cent is used in making tin foil, collapsible container tubes for pastes, type-metal alloys, white-metal alloys (page 249), chemical reagents, etc.

Owing to its comparative costliness, an effort is being made to find substitutes for tin. Food-packing companies are experimenting with lacquered containers as a substitute for those made of tin plate. A phosphorized solder containing 98½ per cent of lead and very little tin has been found to be acceptable in place of the usual lead-tin solder (page 251) in making cans, and for automobile radiators. Cadmium is employed as a partial substitute for tin in Babbitt and bearing alloys.

Zinc

Occurrence.—Because zinc in the metallic form is chemically active, its occurrence in nature is not free but in the form of its compounds. Like lead, it is widely distributed. The sulfide, ZnS, called *sphalerite*, *zinc blende*, and *blackjack*, is the chief ore. This ore generally contains also the sulfides of iron, lead, silver, and cadmium, and it may be accompanied by arsenides, antimonides, calcite, dolomite, and similar substances. Other zinc ores of less importance are *smithsonite* or *zinc spar*, $ZnCO_3$; *zincite*, ZnO; *franklinite*, $(Fe, Zn, Mn)O \cdot (Fe, Mn)_2O_3$; *willemite*, Zn_2SiO_4; *calamine*, $Zn_2SiO_4 \cdot H_2O$. The chief ore-producing countries are the United States, Poland, Mexico, Australia, Spain, Italy, and Canada. In this country the Joplin region deposits of sphalerite (in Kansas, Missouri, and Oklahoma) account for nearly 40 per cent of the

domestic production, and the New Jersey deposits of franklinite and calamine for another 15 per cent. Other deposits are found in Tennessee, Virginia, Idaho, New York, Montana, Utah, Nevada, and New Mexico.

Metallurgy of Zinc.—Sulfide ores of zinc are concentrated by flotation; carbonate, silicate, and other nonsulfide ores are concentrated by magnetic separation, or in a washery by jigging and tabling. A great deal of zinc ore concentrates, like aluminum ore, is transported long distances for smelting. Concentrated zinc blende from Australia, for example, is smelted in quantity in Germany and Belgium. One of the reasons for this practice is that the sulfur dioxide resulting from roasting the blende is converted into sulfuric acid. A ton of rich concentrate, containing only 10 per cent of material other than zinc sulfide, will produce a ton of concentrated sulfuric acid. Unless the zinc is to be recovered from the roasted ore by a process of acid leaching accompanied by the electrolytic deposition of the metal, there is little use for the acid at the mine. It is more economical to transport the blende for smelting to some industrial center where the acid will be consumed in other processes, than it would be to transport the metal and acid to the industrial center. Some of the manufacturers of galvanized steel wire in America smelt the zinc ore at the wire plant. The acid produced is employed in "pickling" (cleaning) (page 429) the steel, and the zinc is used in coating the wire. Few manufacturing processes are more perfectly integrated than this. Even if the sulfur dioxide were of no economic importance, some provision would have to be made to take care of it. It is destructive to vegetation and an active accelerator in the corrosion of metals; consequently, it would become an unendurable nuisance if it were allowed to escape.

General Principles.—There are three ways by which zinc is extracted from its ores: the hydrometallurgical or electrolytic process, the pyrometallurgical or retort process, and the electrothermic or continuous electric furnace process. This last is the most recent development. In the *electrolytic method,* the roasted ore is leached with sulfuric acid, produced from the sulfur dioxide evolved in the roasting as previously noted, and the zinc is recovered from the solution of zinc sulfate by electrodeposition of the metal. Although this method has come into use comparatively recently, during the past few years it has grown rapidly, until in 1937 about 21 per cent of the production in this country was by this method.

There are various ways by which the electrolyte may be prepared. In one of the recent methods, after roasting so that a magnetic decomposition product, zinc ferrite, is formed, the ore is separated into two parts by means of a magnetic separator. The magnetic portion, which contains some zinc oxide in addition to the zinc ferrite, is leached with sulfuric acid. The acid solution of zinc sulfate that results is then neutralized by the use of the non-magnetic portion which consists of pure zinc oxide. Owing to the neutralization, the iron is precipitated as a dense ferric hydroxide, which carries down with it all of the arsenic, antimony, and silica in the ore. The zinc is then deposited electrolytically from the purified solution.

Electrodeposition has important advantages over distillation. The zinc produced is of high purity, and metals may be recovered from the ore that were lost by the older process. The chief plants of the world employing this method are located in Montana, British Columbia, Upper Silesia, and Tasmania.

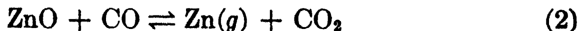
The general principle of the *pyrometallurgical process* of zinc reduction differs from that of most metals; there is no fluxing of the gangue to a melted slag. The zinc oxide, which in the ore may exist as such, or may be produced by roasting the sulfide, is reduced by carbon in the usual manner, but the metal is separated from the unfused gangue by distilling it from the reaction zone. Although the term smelting is employed in the metallurgy of zinc, unless other metals such as lead are also recovered, there is no smelting in the sense in which this term is usually understood.

In order that zinc oxide may be reduced by carbon, it is necessary that the two be intimately mixed and heated to about 1100°C. Because zinc boils at 907°C., the zinc assumes the vapor state at the moment of reduction. Zinc vapor reacts speedily with the oxygen of the atmosphere, and also with carbon dioxide and water vapor, to form zinc oxide. The reduction, consequently, must be carried out in a closed, externally heated vessel, or retort, in the presence of an excess of carbon. It has been shown that, although the over-all reaction in the retort is represented by the equation



$$ZnO + C = Zn(g) + CO, \quad (1)$$

the actual mechanism involves two equilibria:



$$ZnO + CO \rightleftharpoons Zn(g) + CO_2 \quad (2)$$



$$CO_2 + C \rightleftharpoons 2CO \quad (3)$$

At the temperature of the retort the equilibrium in reaction (3) is far to the right, maintaining a low concentration of CO_2 so that reaction (2) proceeds steadily with the production of zinc vapor. It should be noted that both steps involve interaction between a solid and a *gas*, and not between two solids as in reaction (1). Direct reactions between solids are usually slow.

The vapor must be condensed at some temperature above 420°C., the melting point of zinc, or liquid zinc that can be cast will not be obtained. If condensed at a temperature below 420°C., the zinc vapor will solidify in a very finely divided state, called *blue powder* or *zinc dust*. The extremely minute particles of zinc that constitute the blue powder cannot readily be melted to a solid mass. They carry a superficial coating of zinc oxide that prevents them from coalescing. When properly heated, some coalescence may be secured by rubbing, which breaks the coating.

In the operation of this process the retorts are made of earthenware. The charge placed in the retort consists of an intimate mixture of ore and crushed fuel. The percentage of fuel in the mixture will range from 40 to 75 per cent. The fuel in the retort may be noncoking bituminous coal, low in volatile matter, coke breeze, or anthracite coal. The last-named is preferred. The fuel employed under the retorts for heating them may be coal or gas. The retort is connected to an air-cooled earthenware condenser, to which in a few plants is attached a cast-iron prolong, or secondary condenser, also air cooled. The zinc, which vaporizes at the moment of its reduction, emerges from the retort and is cooled in the condenser. In the initial stages of the operation the retorts are too cold; as a result, blue powder is formed. As the condenser becomes warmer, the zinc vapor condenses to liquid, which collects in the bottom of the condenser. Any vapor that escapes into the prolong, being suddenly cooled, also condenses to blue powder. The blue powder collected from the prolong is less oxidized than that from the condenser, and for this reason, when marketed, is always preferred by the buyer. Most of the blue powder, however, is returned to the retort for redistillation. In good practice about 85 to 90 per cent of the zinc in the ore is ultimately obtained in marketable form. Of the zinc distilled, about 60 to 70 per cent is recovered directly in the liquid condition. When removed from the condenser and cast in ingots, it is known as *spelter*.

Because of the prevalence of lead in zinc ores, the spelter is usually contaminated with lead. Since zinc boils at 907°C. and

lead at about 1744°C., in principle, the separation of these two metals by fractional distillation is not difficult, but at the temperature of 1100°C. to which the retort is heated, some lead vapor is carried along with the zinc. When work is being done on argentiferous ores, even silver is volatilized and entrained with the vapor of the other metals. Most of the lead, however, remains in the retort, and lead may therefore be recovered from both the condensate and the retort residue.

The *electrothermic process* was developed in Josephtown, Pa. It is essentially an electric furnace reduction in which the charge of zinc oxide and coke acts as the resistor. A direct reduction of the zinc oxide with the formation of zinc vapor and carbon monoxide takes place. The furnace is a vertical refractory-lined cylinder about 37 ft. in length and 6 ft. in diameter. Near the top of the furnace are three carbon electrodes at 120-deg. angles, and 24 ft. below are three other similarly spaced electrodes. The oxide-coke charge carries the current between these upper and lower electrodes, maintaining an average temperature of 1200°C. The charge is introduced automatically at the top of the furnace and the spent material is discharged by a rotating table at the bottom. The zinc vapor and carbon monoxide leave the furnace through a vapor ring near the top and the zinc is condensed in a special ceramic condenser containing a liquid zinc trap through which the vapors are sucked. The zinc vapor condenses and the carbon monoxide passes through. Liquid zinc is tapped off periodically from the trap and is poured into molds.

In the operation of this process the roasted ores are first put through a sintering treatment. They are mixed with flux, fuel, and water, and heated with gas burners to about 1600°C., with a strong downdraft during the ignition. Incipient fusion occurs with the simultaneous removal of some impurities, principally cadmium and some lead. This sinter is crushed and carefully sized and screened. It is then mixed with coke that has also been carefully sized. This mix is preheated before entering the reduction furnace.

Refining of Spelter.—Spelter may be refined, but a large amount of it is marketed in the condition in which it is received from the condensers. Cadmium and lead, which are the chief impurities, are not objectionable in many instances for galvanizing and brass making, for which purposes much of the zinc is employed. If the spelter is refined, either liquation or redistillation may be used.

In the process of liquation, the zinc is melted at a low temperature in a reverberatory furnace. The nonalloyed and oxidized inclusions rise to the surface and are skimmed off. The lead and the zinc-iron alloy sink to the bottom from whence they are removed by means of a specially devised drain and ladling door. Zinc containing not above 1.25 per cent of lead may be prepared in this way.

Refining by redistillation may be carried out in retorts similar to those of the ordinary reduction furnace. The main difference between the processes is that, in refining, the retorts are heated to a temperature only a little above the boiling point of zinc. This method is very little employed, but a product 99.9 per cent pure can be obtained in this way.

Preparation of Zinc Oxide; Zinc Burning.—During the reduction of zinc ores in the retort process, the zinc vapor, if allowed to escape into the air, will burn and produce dense clouds of zinc oxide, ZnO. The oxide may be collected by allowing it to settle in chambers or by filtering through bags. It is an extremely fine, white powder. In rubber mixtures, such as are used for automobile tires, it is employed extensively to increase the hardness, toughness, and mechanical strength. Under the name of *zinc white,* it is used as a paint pigment (page 552). The best quality of zinc oxide is obtained by burning the vapor produced in the retort distillation of metallic zinc, as described.

By another method, however, known as the *Wetherill process,* the largest proportion of the commercial zinc oxide is produced. An oxidized zinc ore is mixed with coal in a shallow layer on a furnace grate. The air for combustion is supplied under pressure. As the zinc is liberated by reduction of the ore, it vaporizes and burns in the combustion chamber of the furnace. The oxide is conducted away and is collected. If the ore is of the lead-bearing variety, a considerable amount of lead oxide and lead sulfate will be mixed with zinc oxide. As a paint pigment, this product is marketed under the name of "leaded zinc."

In the electrothermic furnaces, if zinc oxide is to be produced instead of the metal, the carbon monoxide and zinc vapor are removed at numerous ports where air is admitted. The zinc burns to ZnO and the CO to CO_2. The zinc oxide is then removed by bag filters.

Grades of Zinc.—According to the amount of impurities present, the A.S.T.M. divides the spelters into four grades, as shown by the following specifications:

STANDARD SPECIFICATION FOR SPELTER

	Lead shall not exceed, %	Iron shall not exceed, %	Cadmium shall not exceed, %	The sum of the Pb, Fe, and Cd shall not exceed, %
A High-grade........	0.07	0.03	0.05	0.10
B Intermediate......	0.20	0.03	0.50	0.50
C Brass special......	0.75	0.04	0.75	1.20
D Prime western....	1.50	0.08		

Grades A, B, and C shall be free from aluminum.

Chemically pure zinc is obtained by distilling purified zinc oxide or precipitated zinc carbonate with pure carbon. It is prepared also by the electrolysis of purified zinc salts. The St. Joseph Lead Company produces in commercial amounts a special grade of lead-free zinc which has a purity of 99.96 per cent.

Properties of Zinc.—The properties of zinc are summarized in Table 28:

TABLE 28.—PROPERTIES OF ZINC

Melting point........................	419.5°C. (787.1°F.)
Boiling point........................	907°C. (1665°F.)
Density............................	7.14 g. per cc. (20°C.)
Electrical resistivity.................	6.0 microhms
Thermal conductivity................	0.268 c.g.s.
Tensile strength.....................	4,000–12,000 psi, cast
	27,900–36,000 psi, rolled
	10,000 psi, hard drawn
Modulus of elasticity................	12.4×10^6 psi

It should be noted that zinc has a fairly low boiling point, 907°C., and that consequently it distills readily so that considerable loss must be allowed for in making alloys containing this metal. Commercial zinc is rather brittle at room temperature, particularly if impure. If heated to between 100 and 150°C., it becomes malleable and ductile and may be rolled into sheets or drawn into wire. It then remains malleable and ductile when cooled to room temperature. If zinc is heated to above 200°C., it becomes brittle again and can be pulverized readily.

The tensile strength of cast zinc is about 5,400 psi; this is found to be increased to about 30,000 psi if rolled and tested in the direction of rolling. Although the strength is even greater transverse

to the direction of rolling, it is more brittle in this direction. When rolled sheet zinc is used to line vats or packing cases, the increased brittleness sometimes becomes apparent; cracks develop in the angles running parallel to the direction of rolling.

Because of its great fluidity when molten, zinc casts well. It shrinks but little on solidifying. Like aluminum, the tensile strength of cast zinc is improved by pouring at as low a temperature as possible, because the crystal structure is finer under such conditions.

Chemical Properties.—When exposed to moist air, the bright luster of zinc is rather rapidly dulled by the formation of a thin film of the basic carbonate, $Zn(OH)_2 \cdot ZnCO_3$. Ordinary commercial zinc does not have a high corrosion resistance where conditions are at all severe. In the air, it burns readily with a bluish-white flame; dense clouds of zinc oxide are formed.

Commercial zinc is soluble in practically all the acids. The dissolving action is hastened by the presence of lead, iron, etc., which have a lower electrode potential (page 414) and are cathodic relative to zinc as explained on page 414. The rate of solution becomes less as the degree of purity increases. Absolutely *pure zinc* will not dissolve at a measurable rate in any of the acids except nitric.

In hot caustic alkalies, zinc is soluble as sodium zincate:



$$Zn + 2NaOH = Na_2ZnO_2 + H_2 \text{ (compare to aluminum)}$$

Uses of Zinc.—As shown by "Minerals Yearbook, 1938," the three chief uses for spelter in the United States are in the production of galvanized ware (page 450), such as sheets, tubes, wire, wire cloth, and shapes; in brass making (page 227); and in the manufacture of sheet zinc. At present the percentages of the total consumption employed for these purposes are about as follows:

Use	Per Cent
Galvanizing	42
Brass	28
Die castings (p. 257)	9
Rolled zinc	15
Other uses	6

A great deal of the rolled sheet zinc finds application in the manufacture of covers for glass jars, and in the making of primary electric cells, such as the dry cell, where it serves both as container and anode. High purity is essential to good performance in the latter case. Sheet zinc is used also for roofs and gutters, washing-machine parts, vat and tank linings, table covers, and pipes.

Minor quantities of zinc are consumed in the manufacture of the paint pigments, French-process zinc oxide (page 169) and lithopone (page 552), and in the production of slush castings. The latter are hollow ornamental castings made by pouring back into the ladle the melted metal from the interior of the casting as soon as that part in contact with the walls of the mold has solidified. By this method, with subsequent plating, the so-called "French bronzes" are made. Etchings for line drawings and similar illustrations are also made of zinc.

In the United States about 8,000 tons of zinc dust (blue powder) are used annually. This is employed chiefly as a pigment in paints, especially in marine paints and in sherardizing (page 450).

Cadmium

Occurrence.—Cadmium is probably the first metal that was not discovered in an ore. It was found in 1817 by Strohmeyer who investigated a sample of zinc carbonate, which, although it contained no iron oxide, was colored yellow. No cadmium ores are known. One cadmium-bearing mineral, *greenockite*, the sulfide (CdS), has been recognized, but no workable deposit of greenockite has ever been discovered.

Cadmium is obtained commercially as a by-product in the metallurgy of zinc and to some extent of lead. It is recovered from the fume produced in roasting zinc blende, from the blue powder formed during zinc distillation, especially in the earlier stages of the process, from intermediate products in lithopone manufacture (page 552), from the tank solutions in the electrolytic method of zinc-ore extraction, from the electrolyte employed in the electrolytic refining of lead, and from lead-furnace fumes. It is more volatile than zinc or lead and may be separated from their metallurgical by-products by redistillation. It may also be recovered by electrolytic methods, or by precipitation with metallic zinc.

About 2,000 metric tons of metallic cadmium are produced annually in the United States, and a considerable amount is imported. The commercial metal, as a rule, is approximately 99.5 per cent pure.

Properties of Cadmium.—Cadmium is a white metal with a bluish tinge, capable of taking a high polish. It is slightly harder than tin but is softer than zinc. It is malleable and ductile, and can be readily rolled and hammered into foil and drawn into wire. If pure, it emits a creaking noise, like tin, when bent. At 80°C. it

becomes so brittle that it can be pulverized under the hammer. The properties of the metal are summarized in Table 29.

TABLE 29.—PROPERTIES OF CADMIUM

Melting point	321°C. (610°F.)
Boiling point	765°C. (1409°F.)
Density	8.65 g. per cc. (20°C.)
Electrical resistivity	7.59 microhms
Thermal conductivity	0.217 c.g.s.
Tensile strength	13,500 psi

Chemical Properties.—Cadmium is not affected by dry air, but in moist air it becomes coated with a grayish-white film of the hydrated oxide. It burns readily at a red heat forming the yellowish-brown oxide CdO. It is readily soluble in nitric, hydrochloric, and sulfuric acids. Although it is noticeably affected by the relatively weak acids, such as acetic and tartaric, it is more resistant than zinc. From solutions of its salts, cadmium is precipitated by zinc.

Uses.—Cadmium is used chiefly in alloys. It is employed especially in low-melting-point alloys (page 257) as a complete or partial substitute for bismuth. Although they are both effective in bringing down the melting point, bismuth has a tendency to make the alloy brittle; cadmium, on the other hand, increases the malleability and ductility. Cadmium is also much cheaper than bismuth. Nearly all the fusible alloys employed for sprinkler heads in automatic fire extinguishers, fire alarms, electric fuses, and safety plugs in boilers contain cadmium. The other metals in such preparations are generally lead, tin, and bismuth. Several of these alloys, although they are strong and can be bent and machined, melt at temperatures much below the boiling point of water. A superior alloy under the name of cliché metal for stereotype plates also has been prepared by substituting cadmium for bismuth. In the jewelry trade cadmium is employed for producing green gold.

Cadmium is now being used as a substitute for tin in solder and in antifriction alloys for bearings. In connection with its use in solders, it must be remembered that even small quantities of cadmium compounds are highly toxic to human beings, and that solders containing this metal, therefore, should not be employed for food containers.

Cadmium is finding some application (page 459) as a rustproofing coating for iron and steel. If heat-treated, the coating forms an alloy with the base metal and exhibits extraordinary

adhesiveness, so that it does not crack or peel off like zinc or nickel when bruised under the jaws of a wrench or pliers. This new use is acquiring importance in the automobile industry. Bolts, nuts, and other small parts employed in automobile manufacture are plated with it, as are also refrigerator trimmings, locks, and wire products. The cadmium coating may be applied by the Schoop metal-spray method (page 447) or by electrodeposition.

Like zinc, cadmium stands above iron in the electromotive force series of metals (page 414) and is therefore able to protect iron in a manner similar to zinc. Cadmium presents a more attractive appearance and retains its luster better than zinc.

MAGNESIUM

Occurrence.—Compounds of magnesium are very abundant and widely distributed. The metal constitutes about 2.1 per cent of the earth's crust; six solid elements, silicon, aluminum, iron, calcium, sodium, and potassium, in the order named, exceed it in quantity.[1] Unlike the ore of aluminum, which element magnesium resembles in physical properties, the compounds of magnesium occur in deposits that are not only extensive, but yield an output eminently suitable for the production of the metal. Of the magnesium minerals, *dolomite*, $CaCO_3 \cdot MgCO_3$, a common rock, is the most abundant. In the United States it is mined[2] in California, Colorado, Illinois, Ohio, Pennsylvania, and West Virginia; it is found also in great quantity in many foreign countries. *Magnesite*, $MgCO_3$, is mined in Austria, Australia, Czechoslovakia, British India, Greece, Italy, Russia, the United States (California and Washington), and other countries. The double chloride, *carnallite*, $KCl \cdot MgCl_2 \cdot 6H_2O$, is found in the Stassfurt deposits of Germany. Some of the other magnesium minerals are *kieserite*, $MgSO_4 \cdot H_2O$; *kainite*, $MgSO_4 \cdot KCl \cdot 3H_2O$; and *brucite*, $MgO \cdot H_2O$. The bittern obtained as a by-product in the purification of common salt in many localities, as at Midland, Mich., is also used as a source of magnesium. The magnesium-salt content of the waters of many inland lakes, notably Great Salt Lake in Utah, is high.

Production of Magnesium.—Metallic magnesium is prepared commercially chiefly by two methods: the chloride and the oxide processes.

[1] GANN, *Ind. Eng. Chem.*, **22**, 694 (1930).

[2] A better quality of this rock is obtained by mining than by quarrying from surface strata.

Until 1927, metallic magnesium was produced from magnesia obtained by calcining magnesite. The process used was similar to the Hall-Heroult method employed in the metallurgy of aluminum. After dissolving the oxide in a bath consisting of the fused fluorides of magnesium, barium, and sodium, the metal was separated by electrolysis. Now, however, the oxide process is no longer used. In both this country and abroad, primary magnesium is obtained by the electrolysis of natural salts. In the United States, magnesium chloride, either recovered in the purification of sodium chloride derived from salt wells or extracted from sea water,[1] is used.

In the chloride process a melted mixture of the chlorides of sodium, potassium, and magnesium is electrolyzed. The presence of the alkali chlorides is necessary to prevent the decomposition of the magnesium chloride during heating. The electrolysis is carried out in an airtight iron vessel, the walls of which act as the cathode, with a centrally located graphite anode, which is protected by a porcelain hood from which the chlorine escapes. As the magnesium is liberated, it rises to the surface and is ladled out.

The metal is refined by remelting it in iron pots and fluxing it with sodium magnesium chloride to remove oxide inclusions. If especially pure magnesium is desired, it is prepared by distillation.

Magnesium is marketed as ingots, sticks, bars, rods, wire, tubes, sheets, ribbon, powder, and in other forms. In 1883, the price of this metal in Europe was about $32 a pound, but in 1902 it had dropped to about $3 a pound. In 1917, the ingot sold in the United States for about $2, but at the present time the price of the 99 per cent pure metal in ingot form is about 30 cts. a pound.

Physical Properties.—Magnesium is the lightest metal used as an engineering material. The tensile strength of the cast metal is 13,000 psi, which is the same as that of ordinary cast aluminum, but when reduction of weight is important, magnesium is preferable because of its low density of 1.74, which is a little less than seven-tenths of that of aluminum. The tensile strength of rolled and annealed magnesium is 25,000 psi, about the same as that of a good quality of gray cast iron. Magnesium is harder than aluminum. It has a somewhat greater need for protection than that metal, and on a strength-weight basis its best alloys are only slightly better than duralumin, one of the best of the aluminum alloys.

[1] The Dow Chemical Company is now constructing a large plant along the Gulf of Mexico to extract magnesium, as well as bromine, from sea water.

In casting magnesium and its alloys, special care is necessary because of its tendency to oxidize readily. Also, because of its lightness, it tends to trap gases during casting and form gas flaws. Because of the readiness with which the hot metal reacts with water, when casting in sand, the molds must be dried. Magnesium is readily machined and under the buffing wheel it takes a high polish. It hardens very rapidly with cold working, but it is suitably plastic and workable at 350°C. Magnesium can be welded, but because it combines with oxygen more readily than any other common metal, a special technique is required. Magnesium may be soldered, but the joints must afterward be protected to prevent them from corroding.

The physical properties of magnesium are summarized in Table 30.

TABLE 30.—PROPERTIES OF MAGNESIUM

Melting point	650°C. (1193°F.)
Boiling point	1107°C. (2024°F.)
Density	1.74 g. per cc. (20°C.)
Electrical resistivity	4.46 microhms
Thermal conductivity	0.37 c.g.s.
Tensile strength	13,000 psi, cast
	25,000 psi, rolled and annealed
Modulus of elasticity	6.25×10^6 psi
Hardness	33 Brinell (500 kg. load, 10 mm. ball)

Chemical Properties.—Magnesium, when pure, does not corrode in ordinary dry air. In moist air, however, it becomes coated with a film of oxide, which is probably partly hydrated and carbonated. The film adheres well and tends to protect the metal beneath. Although magnesium and its alloys are less resistant to corrosion than aluminum and its alloys, the poor reputation of magnesium in this respect has been due largely to the fact that the metal produced in earlier years was very impure; it not infrequently contained as much as 4 to 6 per cent of occluded salts derived from the fused electrolyte. The trapped chlorides were very harmful, so much so that the metal sometimes disintegrated in storage. Substantially pure magnesium has an acceptable corrosion resistance. It may be readily plated with more resistant metals. Lacquers, varnishes, and paints also furnish adequate protection.

In the form of powder or ribbon, magnesium burns readily in air. The light produced by burning magnesium is especially rich in ultraviolet rays, hence its use for flashlight in photographic work. Unless heated to temperatures far above its melting point, mag-

nesium in massive form does not burn readily in air. Magnesium when hot exerts a strong reducing action and serves as a deoxidizing agent for other metals. It is used for this purpose in the metallurgy of both nickel and Monel metal, and to some extent for brass, bronze, and nickel silver. It is able to abstract oxygen from carbon dioxide and under suitable conditions will burn in this gas.

Magnesium decomposes boiling water with the evolution of hydrogen. It dissolves freely in dilute hydrochloric, sulfuric, and nitric acids, but it resists hydrofluoric unless the acid is concentrated. It is not affected by alkalies of any concentration, even when hot, but salt solutions attack it, especially if heated, with the evolution of hydrogen. In all cases its ability to resist the attack of reagents increases markedly as its purity increases.

Uses.—Magnesium readily forms alloys with most metals (not with iron and chromium), and much of it is consumed in this manner. Its employment in the form of sheets, wire, rods, tubes, etc., is noteworthy, however, and its use for these purposes is very rapidly increasing. The ribbon is now used chiefly for the degasification of radio tubes. Its suitability for this purpose depends upon the fact that the heated metal combines not only with oxygen but with nitrogen. The metals with which it is mostly alloyed are aluminum, zinc, manganese, cadmium, and copper, either as binary alloys or with two or more of them together. The tensile strength of these alloys ranges from 20,000 to 50,000 psi, depending partly upon whether they are worked or cast. Since the specific gravity in most cases is well below 1.90, they are eminently suitable for airplane construction. Manganese, which raises the hydrogen overvoltage of the alloy (page 419), increases the corrosion resistance. Approximately 2 per cent of this metal can be alloyed successfully with pure magnesium.[1]

In the powdered form, mixed with an oxidizing agent, such as barium nitrate or potassium chlorate, magnesium is employed in the manufacture of flashlight powder, as has been noted, and in military pyrotechnics for the production of rockets, signals, and flares.

Nickel

Occurrence and Ores.—In the outer crust of the earth, nickel is comparatively rare, but in the core of the earth it is believed to be plentiful. This belief is based partly on the fact that analyses of meteorites show them to contain nickel second in abundance only

[1] Gann, *op. cit.*, p. 698.

to iron. Because meteorites and the earth, as well as the other planets, have a common origin, and because there is some evidence that the core of the earth contains much iron, it seems reasonable to assume that in the earth's central portion nickel also abounds. In the rocky outer layer, nickel is widely distributed, being found on every continent, but deposits of nickel-bearing minerals that are rich enough and plentiful enough to be mined occur in only a few places.

By far the most important known nickel deposits of the world are those of the Sudbury district of Ontario, Canada, where nickel-bearing iron sulfides containing not over 3 per cent of nickel are found. About 90 per cent of the world's annual production of approximately 115,000 metric tons comes from this source. Although imported ores are smelted in the United States, the only nickel now produced in this country from domestic materials is a relatively small quantity in the form of nickel salts recovered during the electrolytic refining of blister copper.

Metallurgy of Nickel.—The details of the smelting process vary, of course, with the nature of the ores, but the general principles involved in the earlier stages are practically identical. The practice is very similar to that described for sulfur-bearing copper ores (page 140), *i.e.*, the ores are roasted to reduce the sulfur content, are then smelted to separate the gangue, and the resulting sulfide matte is bessemerized. The treatment given the New Caledonia ores is interesting. These ores contain no sulfur, and although as a rule the presence of much sulfur complicates a metallurgical process, in this case sulfur, usually in the form of gypsum or iron pyrites, is added to the concentrate prior to smelting. The mixture is then furnaced in much the same way as the Sudbury concentrates.

In the Sudbury district the coarser concentrates are smelted in blast furnaces, and the finer ones at a reverberatory plant. The matte delivered by the smelting furnace is then bessemerized to oxidize the iron. The iron oxide combines with a siliceous flux added for this purpose and enters the slag. The bessemer matte consists chiefly of copper and nickel sulfides.

Extraction of Nickel from Matte.—There are two principal methods for extracting nickel from the copper-nickel matte. One is the method employed by the International Nickel Company at Port Colborne, Ontario, which is sometimes called the Orford process, and the other is the Mond process used at Clydach, Wales.

In the International Nickel Company's method, the matte is charged into a blast furnace with coke and sodium sulfate, which, by the reducing action of the carbon, is converted into sodium sulfide. The output of the blast furnace is poured into pots and allowed to cool. During solidification the mass separates into two well-defined layers. The upper layer carries the bulk of the sodium and copper sulfides; the bottom layer contains the bulk of the nickel sulfide. The two layers are separated mechanically. The top layer is "blown" in a bessemer converter to blister copper. The bottom layer, after suitable treatment, is roasted to black nickel oxide, which is then reduced to metallic nickel in an open-hearth furnace. From the melted nickel, pigs, shot, and anodes are produced. The anodes are employed by electroplaters.

In the Mond process employed by the British nickel industry, "nickel bottoms" of the Orford process, shipped from Ontario to Wales, are ground to a fineness sufficient to pass a 60-mesh screen and then are calcined to convert the sulfides to oxides, which in turn are leached with sulfuric acid. The copper oxide is thus converted into copper sulfate, which is recovered and sold as such; the nickel oxide remains undissolved. The nickel is recovered from the nickel-oxide residue by an ingenious and interesting method. The oxide, heated to 300°C., is reduced to metallic nickel by hydrogen obtained from water gas (page 59). The reduced metal, after cooling to ordinary room temperature, is by treatment with carbon monoxide converted into nickel carbonyl, $Ni(CO)_4$, a liquid. When a stream of nickel carbonyl vapor is later passed through a tower filled with nickel pellets heated to 180°C., the carbonyl breaks down into nickel and carbon monoxide gas. The nickel deposits on the pellets and the carbon monoxide is returned to the reaction chamber where the nickel carbonyl is formed. The nickel pellets are withdrawn continuously from the bottom of the tower and are recharged at the top. The constant friction of the pellets against each other detaches small particles, which, acting as nuclei, grow into new pellets by accretions of nickel from the carbonyl. Before recharging, the pellets are screened, and only the smaller ones are returned to the tower. Those that are oversize are marketed. The nickel produced by this process is about 99.8 per cent pure.

Monel Metal.—If the matte from the converters is of the proper composition, it is dead-roasted to eliminate the sulfur, leaving a mixture of oxides of nickel and copper and a small amount of iron.

This mixture is fused directly in a reverberatory furnace with coke as a reducing agent. A nickel (67 per cent), copper (28 per cent) alloy, called Monel metal, is produced, which has important industrial applications (page 246).

Malleable Nickel.—The form of the metal marketed as malleable nickel is prepared by deoxidizing and recarburizing in a manner very similar to that employed for steel (page 302). The deoxidation is effected by adding manganese, in the form of ferromanganese, followed by magnesium. Only a small quantity of magnesium is employed, and it must not be used in excess. By the use of charcoal, the carbon content is brought to an amount between 0.1 and 0.3 per cent. These additions are made to the metal while in the crucible or ladle just prior to casting. Only that which is sold as malleable nickel is treated in this manner.

Properties and Uses.—Nickel is a silvery white metal capable of taking a high polish. It is almost as hard as soft steel. When it contains a small amount of carbon, as discussed above, it is quite malleable. In fact, it may be satisfactorily rolled with as little as 0.005 per cent of carbon. It is somewhat less ductile than soft steel, but small amounts of magnesium improve the ductility considerably.

Nickel is resistant to the attack of most acids, but it dissolves readily in nitric acid. It is very permanent upon exposure to the atmosphere, and is extensively used to plate iron and brass as a protective coating.

Nickel is ferromagnetic below 360°C. Its properties are summarized in Table 31.

TABLE 31.—PROPERTIES OF NICKEL

Melting point	1452°C. (2656°F.)
Boiling point	2732°C. (4950°F.)
Density	8.85 g. per cc.
Electrical resistivity	10.9 microhms
Thermal conductivity	0.140 c.g.s.
Tensile strength	70,000 psi, rolled and annealed Up to 140,000 psi, hard rolled
Modulus of elasticity	30×10^6 psi

Practically all of the nickel produced is used in a variety of extremely important ferrous and nonferrous alloys. These will be described in Chaps. V and VII. An analysis of the consumption of nickel[1] in this country is given in the following table in which the figures are in per cent.

[1] "Minerals Yearbook, 1938," U.S. Bureau of Mines, p. 553.

	Per Cent
Steels (construction, stainless, and other corrosion- and heat-resisting steels and steel castings, pp. 361, 364)	55
Monel, malleable nickel, nickel clad, and Iconel	12
Nickel-copper alloys and nickel silvers (p. 246)	10
Electroplating (p. 446)	10
Nickel cast iron (p. 382)	5
Heat-resistant and electrical-resistant alloys (p. 247)	3
Nickel-brass, bronze, and aluminum alloys	2
Nickel-iron alloys	1
Nonmetallic materials (salts, storage batteries, catalysts)	1
Miscellaneous	1

Cobalt

Although cobalt has some uses for which it would be difficult to find an equally acceptable substitute, industrially it ranks among the metals of only minor importance. The total yearly world production is not over 3,000 tons. The chief producers are Northern Rhodesia, Belgian Congo, French Morocco, Burma, Ontario, and Australia. The Congo supply comes from veins of cobalt, copper, and iron sulfides; the Ontario ores are arsenides and arsenosulfides; the Australian ores are arsenosulfides. The chief minerals are *cobalt bloom*, $3CoO{\cdot}As_2O_5{\cdot}8H_2O$; *cobaltite*, CoAsS; and *smaltite*, $CoAs_2$. Some of the cobalt on the market is obtained as a by-product from nickel ores.

Properties and Uses.—Cobalt resembles nickel in many of its properties. Its silvery white color is similar, but it can be distinguished from nickel by its slight bluish cast. It is somewhat harder than nickel and, for this reason, would be superior for plating. Another apparent advantage is that the plate can be deposited 10 to 15 times as rapidly. Cobalt is magnetic but, unlike nickel and iron, it retains its magnetism even at a white heat; the transition from magnetic to nonmagnetic form is at 1150°C. In the atmosphere, cobalt resists corrosion very well. It dissolves only slowly in all acids except nitric, by which it is rapidly attacked.

The properties of cobalt are summarized in Table 32.

TABLE 32.—PROPERTIES OF COBALT

Melting point	1490°C. (2714°F.)
Boiling point	2890°C. (5250°F.)
Density	8.9 g. per cc.
Electrical resistivity	9.7 microhms
Thermal conductivity	0.165 c.g.s.
Tensile strength	33,000 psi, cast 63,000 psi, hard drawn

The chief use of cobalt is in the making of Stellite (Co-Cr-W), a group of alloys consisting essentially of cobalt and chromium. In a high-speed, cutting-tool alloy of phenomenal hardness that has been recently developed, cobalt serves as a cementing material for tungsten carbide (page 377). Stellite and cemented tungsten carbide are not steels, but some of the high-speed steels, as well as some corrosion-resistant steels, contain cobalt. It is employed also in making steel for permanent magnets. The magnetic coercive force of the cobalt steel is from two to five times that of the commonly used tungsten or chromium steels but, because of the relatively high price of cobalt, such steels, compared to others, cost from four to ten times as much.[1]

Cobalt oxide is employed to a considerable extent in the ceramic industry. Glazes and enamels contain it. In enameling ironware, cobalt oxide renders exceptional service in causing the enamel to adhere to the metal (page 461). Blue glass is made by the addition of cobalt oxide.

Cobalt linoleate and tungate (page 569) are very serviceable as driers for paint and varnish oils, especially oil from the soybean.

The cobalt imported annually for consumption in the United States, as ore, metal, and oxide, does not exceed about 1,200 tons.

Manganese

Importance of Manganese.—The steel produced by the bessemer process at the time of its invention, which was announced to the British Association in 1856, was devoid of malleability. The foundation for the importance of manganese as an industrial metal was established when Bessemer was convinced by Mushet that the toughness of the new steel would be greatly improved by the addition of manganese. At the present time, there is practically no steel made by any process that does not receive the manganese treatment (page 285). The world's total annual production of high-grade manganese ore is now between 4 and 6 million tons, over half of which is produced by Russia. Most of this manganese is consumed by the steel-making industry.

Producers and Consumers.—Manganese ores are widely distributed, but about 80 per cent of the world's total output comes from Russia, India, Brazil, the Gold Coast of Africa, and Cuba. It is found as the dioxide, MnO_2, *pyrolusite*. Comparatively small

[1] Sanford, "Some Principles Governing the Choice and Utilization of Permanent Magnet Steels," *Nat. Bur. Standards, Sci. Paper* 567, p. 557.

amounts are produced in the United States, Italy, China, Chile, and the Dutch East Indies. Although the United States produces less than 1 per cent of the world's output, it consumes about 20 per cent, or close to a million tons annually. Other large importers are France, Germany, Great Britain, Belgium, and Japan.

Production of Metallic Manganese.—As has been stated before, the largest part of all the manganese produced is consumed in the manufacture of steel. For use in this industry (page 304), the manganese is first prepared in the form of two intermediate alloys, ferromanganese and spiegeleisen. Ferromanganese contains from 75 to 81 per cent of manganese, from 5 to 6 per cent of carbon, and the remainder chiefly iron. Similarly, spiegeleisen is an iron alloy containing from 15 to 20 per cent of manganese and about 5 per cent of carbon. Both alloys are manufactured by smelting the ore in a blast furnace of the same type as that employed in the production of pig iron (page 264).

For spiegeleisen the furnace practice is almost the same as in the iron industry, but for ferromanganese the furnace is burdened in a somewhat different manner. Because the manganese oxide has a tendency to enter the slag, a higher proportion of limestone is employed in the charge than is used in the smelting of iron ore. The slag is thus made more "limey" or basic, and manganous silicate is less likely to form. Because the manganese ore is more refractory than iron ore, a higher coke ratio also is maintained than in the production of pig iron. At the high temperature required for smelting the ore, manganese shows a marked volatility. A loss of as much as 15 per cent of the metal may result from this cause.

By the Thermit process (page 138) metallic manganese may be obtained almost entirely pure. The absence of carbon in manganese so obtained is a point worthy of comment. By using this purer variety, high-manganese steel may be manufactured that is much softer and far more workable than that made from the alloy reduced by carbon.

By a patented process, ferromanganese produced in a blast furnace may also be decarbonized by treatment with manganese dioxide in an electric furnace. In this method the carbon content may be reduced from 5 or 6 to less than 1 per cent.

Properties and Uses.—Manganese is hard, steel gray, and brittle. It lacks malleability and toughness and is not employed in constructional work except in alloys. The properties of the metal are summarized in Table 33.

TABLE 33.—PROPERTIES OF MANGANESE

Melting point	1220°C. (2228°F.)
Boiling point	2152°C. (3905°F.)
Density	7.2 g. per cc.
Electrical resistivity	5 microhms

Upon exposure to the atmosphere, manganese oxidizes in a manner similar to iron, but more readily. It dissolves freely in the common mineral acids, even when dilute, with the formation of manganous salts. It is soluble in acetic acid. It reacts with boiling water to produce the hydrated manganous oxide and hydrogen. If the metal contains the carbide Mn_3C, when moistened with water methane and hydrogen are produced.

The extensive use of manganese in the manufacture of iron and steel is due to the readiness with which it can transpose the ferrous oxide and sulfide into the corresponding manganous compounds. The resulting manganous compounds are only slightly soluble in the melted metal and are, therefore, carried away by the slag.

Among the common nonferrous alloys of manganese are manganese bronze, manganin, nickel silver, and manganese brass. Manganese bronze contains on an average 16 to 17 per cent of manganese in copper. Manganin, which contains 12 to 15 per cent of manganese, about 4 per cent of nickel, and the remainder copper, is used for electrical resistances. With a small per cent of manganese, nickel silver is harder and tougher than the usual variety (page 239). Manganese brass is described on page 233.

In the form of the oxide, manganese is employed as a coloring agent in the ceramic industry and for the purpose of discharging the color produced by iron in the manufacture of glass. The dioxide is used as a depolarizing agent in the manufacture of Leclanché and dry cells.

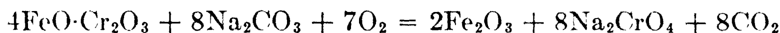
CHROMIUM

Occurrence.—The only commercial ore of chromium is *chromite*, or *chrome iron ore*, which has the formula $FeO \cdot Cr_2O_3$. It is a heavy black mineral with a Cr_2O_3 content varying from 33 to 53 per cent. The principal impurities are SiO_2, Al_2O_3, and MnO. It is usually concentrated by gravity methods. Over a million tons are used in this country annually, of which only 2,000 tons are produced here (in California). The remainder is imported chiefly from Africa, with smaller amounts from Cuba, Greece, New Caledonia, and Turkey.

Treatment of Chromite.—The uses for chromium ore may be classified under four general headings: (1) as a refractory (page 113), (2) for the manufacture of chromium compounds such as chromates, bichromates, and chrome alum, (3) for the production of ferrochrome (page 186), (4) for the production of metallic chromium.

For use as a refractory material, particularly in the steel industry, the ore, after suitable concentration, is mixed with a little lime and made into bricks. For furnace linings in the steel industry no equally satisfactory substitute for chromite is known. Its properties as a refractory material are described on page 117.

Among the chromium compounds, the chromates of sodium and potassium, and chromic oxide are important. In the production of the chromates, the ore is roasted with sodium or potassium carbonate in the presence of air. The reaction may be represented as follows:



$$4FeO \cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

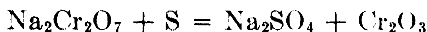
If the bichromate is desired, it is prepared by treating the chromate with sulfuric acid, thus,



$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

Because the sulfate has the lower solubility, it crystallizes first from the solution. The bichromate is recovered from the remaining liquid.

Chromic oxide is obtained by heating sodium bichromate with sulfur in an iron vessel. The following reaction occurs:



$$Na_2Cr_2O_7 + S = Na_2SO_4 + Cr_2O_3$$

Chromic oxide formed in this way is green and, having been ignited, is insoluble in water. It may be employed in the production of metallic chromium by the Thermit process. Chromium trioxide, CrO_3, in the form of red crystals that dissolve readily in water, may be formed by treating dry sodium chromate with concentrated sulfuric acid. The following reaction takes place:



$$Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + H_2CrO_4$$

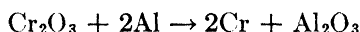
The concentrated sulfuric acid immediately dehydrates the chromic acid with the formation of chromium trioxide which precipitates. When this oxide is dissolved in water, it rehydrates and again forms chromic acid. A large amount of chromic acid is consumed by the chromium electroplating industry (page 187).

In the production of ferrochrome, an alloy of iron and chromium, containing 60 per cent of chromium or more, the ore is reduced with carbon in an electric furnace. The theoretical reaction may be represented as follows:



$$FeO \cdot Cr_2O_3 + 4C = Fe + 2Cr + 4CO$$

Because metallic chromium combines readily with carbon, however, a considerable amount of it does not appear in the metallic form as called for by the equation, but in the form of chromium carbide, Cr_3C. In the steel industry, ferrochrome with a high-carbon content is not desired. The quality and price of the alloy, therefore, are inversely proportional to the carbon content. By treatment with chromite under a basic slag of lime and a little feldspar, ferrochrome may be largely decarbonized (*cf.*, ferromanganese, page 183). Another method sometimes employed for the production of low-carbon ferrochrome is the Thermit reaction (page 138). Metallic chromium also is produced from chromic oxide by the Thermit process, as follows:



$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

Chromium that is 99.5 per cent pure is obtained by this method; it contains some aluminum.

Properties of Chromium.—Chromium is a bluish-white metal, harder than glass. When polished it shows a brilliant platinumlike luster which it retains indefinitely. The ordinary form of the metal is brittle, but electrolytically deposited chromium is hard and malleable. The properties of the metal are summarized in Table 34.

TABLE 34.—PROPERTIES OF CHROMIUM

Melting point	1550°C. (2822°F.)
Boiling point	2477°C. (4490°F.)
Density	7.138 g. per cc.
Electrical resistivity	13.1 microhms
Thermal conductivity	0.65 c.g.s.

Chromium is not attacked by atmospheric oxygen at ordinary temperatures, but at high temperatures it burns to the green trioxide, Cr_2O_3. It dissolves slowly in cold hydrochloric acid, but rapidly in the hot acid. In cold, dilute sulfuric acid it dissolves only slowly also, but in the hot, concentrated acid it dissolves rapidly with the evolution of sulfur dioxide. It is slowly attacked by cold, dilute nitric acid, but hot concentrated nitric acid does not affect it.

Concentrated nitric acid renders it passive (page 431). When in the passive state it does not dissolve in the ordinary reagents, *e.g.*, hydrochloric acid. Chromium is made passive also by chromic acid and by exposure to air. The fact that air makes it passive accounts largely for its outstanding success as a coating for other metals and as a constituent of "stainless" alloys (page 364).

Uses of Chromium.—Almost half of the chromium output is produced in the form of ferrochrome, which is employed chiefly in the manufacture of alloy steels (page 358). Chromium is used in steel because it imparts not only hardness but toughness, a combined effect that is unusual. Of no less importance is the fact that chromium has a marked effect in increasing the resistance of steel to corrosion. Much of the rustless iron and rustless steel now on the market contains chromium (page 370). In the use of this metal lies perhaps the solution of the age-old problem of the production of a workable, low-carbon steel that will satisfactorily withstand corrosion.

Nichrome is an alloy of chromium and nickel; sometimes it contains iron. The composition of the following alloys is representative: (1) chromium 20 per cent, nickel 80 per cent; (2) chromium 15 per cent, nickel 60 per cent, iron 25 per cent. These alloys, known also by the trade name of "Chromel," have a high electrical resistance and do not oxidize materially when hot. They are employed in the winding of electric resistances and heating units. Chromium is also a component of Stellite (page 182).

Electroplating with Chromium.—The brilliant, platinumlike finish that may be imparted to chromium, and the passivity of the metal in air, render it suitable as a decorative and protective coating for other metals. Its employment for this purpose, particularly in the automobile industry, has attracted a great deal of attention.

In electroplating with chromium, the electrolyte consists of a solution of chromic acid, H_2CrO_4, to which chromic sulfate, $Cr_2(SO_4)_3$, or other salts, such as the borate and phosphate, have been added. Chromium sulfate especially has a very beneficial effect. The percentage of chromic acid employed in the electrolyte varies considerably, but 25 per cent may be considered to be a representative concentration. The amount of the sulfate present will probably not greatly exceed $1/100$ of the amount of the chromic acid, but according to Keeney,[1] it is apparently necessary to have

[1] LIDDELL, "Handbook of Non-ferrous Metallurgy," Vol. II, p. 1261, footnote, McGraw-Hill Book Company, Inc., New York (1926).

chromium present in two valences in the electrolyte in order to secure good results.

In producing the deposit, a very high current density is employed; it generally ranges from 100 to 125 amp. per sq. ft. If a very low current density is used, no chromium whatever is deposited; the electron stream merely changes the hexavalent chromium to trivalent chromium. With the high current density that is employed, in addition to the deposition of chromium, hydrogen is evolved freely at the cathode. Lead anodes are used but only a little lead dissolves.

Owing to the conditions under which it is deposited, chromium plate is porous. When used alone it is not a good protection against corrosion. According to Schneidewind,[1] this is not surprising when it is considered that the best plate for decorative purposes is put on in about 3 min. and is only 2/100,000 in. thick. He states further that the average plate in many job shops is applied in 30 to 40 sec. and is only 2/1,000,000 in. thick. The reason given by Schneidewind for not applying a heavier coating is that a heavier plate not only greatly increases the cost but also defeats its own purpose because a system of fine cracks and other imperfections develops through which corrosion sets in.

Chromium can be deposited directly upon copper, brass, nickel, cobalt, steel, and most other metals, but owing to the fact that the usual decorative chromium plate is not a sufficient protection for iron and steel and because of their tendency to corrode, these metals are first plated with copper and then with nickel or with the latter alone, prior to the application of the chromium. In order to secure the brilliance desired in the finished plate, the base metal is polished to a high luster before it is placed in the chromium plating bath.

In commenting upon the abrasion resistance of chromium plate, Schneidewind states[2] that, although chromium itself, if applied in a heavy layer on a hard backing, is so hard that only the diamond or carborundum will affect it, decorative chromium plate is not hard. This lack of hardness results from the fact that the layer is very thin and is usually applied over comparatively soft metals. Usually, decorative chromium plate can be easily punctured or scratched.

One of the chief virtues of chromium plate lies in the fact that it does not tarnish or show spots, even in rainy weather. In view

[1] "Commercial Chromium Plating," Dept. Engineering Research, *Univ. Mich.*, *Circ. Ser.* 3, p. 9, January, 1930.

[2] *Loc. cit.*, p. 10.

of its superior qualities in this respect, the slightly higher cost as compared to nickel plate is of little consequence.

TUNGSTEN

About half of the tungsten supply of the world is produced by China. Most of the ore apparently comes from Kiangsi and neighboring southeastern provinces. Little is known definitely about the character and extent of these deposits; very few white men have even seen the larger part of them, and no authoritative reports are known to have been issued. All that can be said with certainty is that China produced in 1937 about 18,000 tons of tungsten ore carrying 65 to 70 per cent of tungstic oxide, WO_3.[1]

As a producer of tungsten, Burma ranks next in importance to China, and the United States is third. About 3,000 tons of 60 per cent concentrates were produced in this country in 1937; more than twice this amount was imported. Small quantities of tungsten ores are produced also by the Malay States, Portugal, and Bolivia.

Ores.—The most important tungsten ore is a ferrous manganese tungstate called *wolframite*, $(Fe, Mn)WO_4$. The ratio of iron to manganese varies; depending upon this fact, the ore is called by various names. The high-iron and low-manganese ore, for example, is known as *ferberite*. Calcium tungstate, called *scheelite*, $CaWO_4$, is also an important source of the metal. Other minerals are the lead and copper tungstates, and the trioxide called *wolfram ocher*, WO_3.

Ferrotungsten.—From a tonnage standpoint the main use of tungsten is in the manufacture of steel, especially steel for tools employed at high cutting rates. For the manufacture of this steel either ferrotungsten or tungsten powder may be used.

In the production of ferrotungsten, the process is similar to that described for ferromolybdenum (page 192). If the ore is ferberite, no preliminary treatment other than concentration is necessary. The ore is reduced by carbon in crucibles placed in oil-fired furnaces, or is reduced in an arc-type electric furnace. If the ore does not contain sufficient iron, it is added in the form of scrap. The material produced in this country contains about 70 to 80 per cent of tungsten and less than 0.75 per cent of carbon.

Metallic Tungsten.—To produce tungsten metal suitable for drawing into wire or rolling into sheets, very pure tungstic oxide must first be prepared from the ore. The pulverized ore is mixed

[1] "Minerals Yearbook, 1938."

with excess Na_2CO_3, ground to 100 mesh and heated in a reverberatory furnace at 800°C. The soluble sodium tungstate, Na_2WO_4, formed is then extracted with hot water. From this solution the insoluble calcium tungstate, $CaWO_4$, is precipitated by the addition of $CaCl_2$. This, in turn, is converted to insoluble tungstic acid, H_2WO_4, by treatment with HCl. After filtering and washing, this material has a purity of about 99.5 per cent. The final step in the purification consists in dissolving the tungstic acid in concentrated ammonia and evaporating to crystallization of ammonium paratungstate, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$. From this salt the tungstic acid is reprecipitated by HNO_3. This final treatment may be repeated for additional purification, and the tungstic acid is then ignited to the oxide WO_3, which will analyze 99.94 to 99.96 per cent pure, with an iron content less than 0.02 per cent.

The pure oxide is placed in nickel boats in a tube furnace and reduced to metallic tungsten in a stream of hydrogen at 1200°C. Since the melting point of the metal is very high (3390°C.), the product of the reduction is a gray unfused powder. The earlier workers found it a very difficult problem to produce a workable mass of the metal. After long experimentation it was found that the most feasible method for compacting the granules was to work them mechanically while very hot. For this purpose, the finely divided metal is placed in steel dies and pressed hydraulically to 300 tons. The granules of the resulting bar are then caused to coalesce by placing the bar in an atmosphere of hydrogen and heating it by means of its resistance to the flow of an electric current. Toward the close of the process the temperature is raised to a point not far below the melting point of tungsten. As a result, the particles are joined and a definite crystalline structure is developed. By means of repeated heating and swaging or hammering, the sintered bar is worked into a slender rod. Although at first the bar is very brittle and weak, with repeated working the strength and toughness increase so much that it may be drawn through dies to form wire. For very fine wire, such as required for lamp filaments, a series of as many as 100 dies formed of diamonds, each with an aperture slightly smaller than the one preceding, are employed. If sheet or plate is desired, the bar is rough-forged under the hammer, and then is reduced to the specified gauge by means of high-speed rolls.

If metallic tungsten is to be used merely for the production of alloys or carbides (described below), extreme purity is not necessary. A metal of better than 98 per cent purity is made by direct

precipitation of tungstic acid from the Na_2WO_4 solution, already described, by the addition of hydrochloric acid. This is ignited to WO_3 and reduced with powdered charcoal in crucibles heated to 1800°C.

Properties of Tungsten.—Tungsten is silvery white in color. It oxidizes in air at a red heat, forming the yellow oxide WO_3. Dilute acids are practically without action on the metal, but hot concentrated sulfuric and hot hydrochloric acids attack it slowly.

In the form of fine-drawn wire, tungsten possesses the highest tensile strength of all known materials. In addition it has the highest melting point of all elements except carbon. Even at a white heat it retains its rigidity and because of its extremely low vapor pressure sublimes only slowly even in a high vacuum. The properties of the metal are summarized in Table 35.

TABLE 35.—PROPERTIES OF TUNGSTEN

Melting point	3390°C. (6130°F.)
Boiling point	5930°C. (10700°F.)
Density	19.3 g. per cc.
Electrical resistivity	5.48 microhms
Thermal conductivity	0.476 c.g.s.
Tensile strength	590,000 psi
Modulus of elasticity	60×10^6 psi

Economic Value of Tungsten.—No other metal produced in such small quantity has so great an industrial importance as tungsten. Because of the convenience, comforts, and luxuries it provides to the present type of civilization, its importance is comparable to that of lead and zinc, and is exceeded only by that of iron and copper.

As has been indicated before, the two main uses for tungsten are in the manufacture of high-speed tools (pages 377 and 379) and filaments for lamps. It is estimated that the substitution of tungsten-bearing tools for carbon-steel tools and of tungsten-filament lamps for carbon-filament lamps saves the people of the United States not less than 2½ to 3 billion dollars each year. The enormous saving that is brought about by the use of tungsten-alloy tools is made possible by the fact that one man is able to perform the work of several men in the turning, planing, and boring operations required in the fabrication of articles produced by the metal-working industries. Not only are less time and labor involved, but the mechanical equipment and the space needed to house it are less.

The economy in the use of tungsten-filament lamps rests upon the fact that they require only 1.25 watts per candlepower, instead

of the 3.25 watts consumed by the older type of lamp in furnishing the same illumination. It has been calculated that if the artificial light used in the United States were produced by carbon-filament lamps, an additional expenditure of 2 billion dollars would be required. That tungsten is able to replace carbon in this efficient manner depends not only upon its high melting point, but upon its rigidity at high temperatures, its low vapor pressure, and its relatively high electrical resistance.

In addition to their admirable performance in the lighting field, tungsten filaments demonstrate their usefulness in radio tubes and X-ray tubes. When employed in the latter, such filaments make possible the generation of rays so penetrating that almost instantaneous X-ray photographs of the body can be taken. Moreover, by the use of these rays, a new science has been developed, that of the study of atomic and crystal structure, as well as the inspection of the interior of metals. In steel, for example, segregation, gas flaws, shrinkage flaws, slag and oxide inclusions, and other faults may be detected without physical alteration of the specimen.

The one other purpose for which tungsten in the pure state finds extensive application is the making of the electrical contact points used in the ignition systems of internal-combustion engines. For this purpose it has almost completely replaced platinum at a tremendous saving in cost.

Important alloys of tungsten are discussed on pages 248, 377.

Molybdenum

Occurrence.—The chief molybdenum ore is the sulfide, *molybdenite*, MoS_2. It is a soft, opaque, dark-gray, graphitelike or micalike mineral. It occurs in flakes that cleave readily. *Molybdite*, $Fe_2O_3 \cdot 3MoO_3 \cdot 7\frac{1}{2}H_2O$, is a decomposition product produced by the weathering of molybdenite. *Wulfenite*, $PbMoO_4$, is also an important source of molybdenum.

Over 90 per cent of the world production of 16,000 tons of molybdenum was supplied by the United States in 1937. Nearly 80 per cent of this domestic production came from the Climax mine in Colorado. Small amounts were produced in Arizona, Idaho, Nevada, and New Mexico.

Ferromolybdenum.—The chief use of molybdenum is in the manufacture of ordnance and high-tensile steels (page 361). For this purpose the metal is supplied in the form of ferromolybdenum, an iron-molybdenum alloy containing 50 to 60 per cent of molyb-

denum. The ore, molybdenite, is concentrated by flotation and is then roasted to the oxide, MoO_3. This is then reduced by carbon in the electric furnace with the addition of scrap iron. The product usually contains less than 2 per cent of carbon.

Metallic Molybdenum.—Metal of high purity is used in radio and X-ray tubes and for support wires in electric-light bulbs. It is made by a method similar to that used for tungsten. The oxide from the roasting of the ore is converted to ammonium molybdate and this is purified by crystallization. Ignition of this salt gives an oxide of high purity. This is reduced to a metallic powder by hydrogen and is pressed, swaged, and drawn into wire as with tungsten.

Properties of Molybdenum.—Molybdenum is quite similar to tungsten in appearance and in properties. The melting point is lower, however, and the tensile strength much smaller. The properties of the metal are summarized in Table 36.

TABLE 36.—PROPERTIES OF MOLYBDENUM

Melting point	2622°C. (4751°F.)
Boiling point	4804°C. (8679°F.)
Density	10.2 g. per cc.
Electrical resistivity	4.77 microhms
Thermal conductivity	0.350 c.g.s.
Tensile strength	260,000 psi
Modulus of elasticity	50.2×10^6 psi

VANADIUM

Occurrence and Ores.—The largest and richest vanadium deposit known occurs at Minasragra, Peru. The ore found there, called *patronite*, has a composition that may be represented approximately by V_2S_9. It occurs in conjunction with iron pyrite, free sulfur, and carbonaceous matter. The presence of the carbonaceous matter is interesting. It may be associated with the fact that the ashes of some Peruvian coals contain nearly 50 per cent of vanadium pentoxide, and that about 1 per cent of the vanadium output of Peru is derived from the ash of a native asphaltite.

The countries next in order in the production of vanadium are South-West Africa mandate, United States, and northern Rhodesia. Together their output is roughly equal to that of Peru. The chief African ores are *descloizite*, $(Pb, Zn)(VO_3)_2$, a lead-zinc vanadate; and *vanadinite*, $Pb_5(VO_4)_3Cl$, a lead chlor-vanadate. In the United States *roscoelite*, a vanadium mica of complex and somewhat indefinite composition, approximately represented by the

formula $H_8K_2(Mg, Fe)(Al, V)_4(SiO_3)_{12}$, and *vanoxite*, a hydrous vanadium oxide are found in Colorado; *carnotite*, a potassium uranyl vanadate, $K_2O{\cdot}2UO_3{\cdot}V_2O_5{\cdot}3H_2O$, is mined in both Colorado and Utah. Commercially, roscoelite is second in importance to patronite as a source of vanadium.

The United States produces about half of the vanadium consumed here; the remainder is imported mainly from Peru.

Ferrovanadium.—The chief use of vanadium is in the manufacture of vanadium steel. For this purpose an alloy, ferrovanadium, containing 30 to 40 per cent of vanadium, less than 0.5 per cent of carbon, and small quantities of other elements, in addition to the iron, is used. Formerly, the ferrovanadium was almost entirely prepared by reducing the oxide in the presence of iron turnings by the use of aluminum or silicon, a modification of the Thermit process, but recently a method has been developed for electric-furnace reduction with carbon. In the new process, the mixture of ore and flux is fed through a zone of extremely high temperature between closely spaced, graphite electrodes. The pentoxide is reduced directly to the metal and the use of the costly reducing agents, aluminum and silicon, is avoided.

Metallic Vanadium.—The preparation of pure vanadium is difficult, and very little is produced commercially. For obtaining the metal, acceptable methods are the reduction of the dichloride with hydrogen, and the electrolysis of vanadium trioxide in fused calcium vanadate.

Vanadium is silvery white in color, is harder than quartz, but is sufficiently malleable and tough so that, when heated to a suitable temperature, it may be rolled and hammered into rods and drawn into wire. The metal is susceptible to a high polish and does not tarnish in air. When heated rapidly in a stream of oxygen, vanadium burns brilliantly. When burning in air, it combines not only with oxygen but with nitrogen; a mononitride is formed. Vanadium is insoluble in hydrochloric acid or in solutions of the alkalies. It is slowly attacked by concentrated sulfuric acid, but is readily soluble in nitric acid, both dilute and concentrated. The properties of vanadium are summarized in Table 37.

TABLE 37.—PROPERTIES OF VANADIUM

Melting point	1710°C. (3110°F.)
Boiling point	3000°C. (5432°F.)
Density	5.68 g. per cc.
Electrical resistivity	26 microhms

Uses of Vanadium.—As has been indicated before, the chief use of vanadium is in the manufacture of alloy steels (page 361). Nonferrous alloys of vanadium are those of copper and aluminum, from which excellent castings may be made. One of the new applications of vanadium is its use in the form of the pentoxide, instead of platinum, as a catalyst in the manufacture of sulfuric acid. Unlike platinum, vanadium pentoxide is not poisoned by arsenic and hydrochloric acid. The pentoxide serves to catalyze reactions other than the conversion of sulfur dioxide to the trioxide, and compounds of vanadium other than the pentoxide may be employed. Vanadium resinate has proved to be a superior drier for paint and varnish oils.

Bismuth

The principal producers of bismuth, in order of importance, are the United States, Peru, Mexico, Spain, Canada, Germany, and Japan, accounting for the total yearly production of only 2,000 tons. It occurs in nature mainly in the metallic state, but the oxide, *bismuth ocher*, Bi_2O_3, and the sulfide, *bismuth glance* or *bismuthite*, Bi_2S_3, are also of commercial importance. Bismuth ores are seldom found pure, but generally are associated with the ores of other metals. A considerable part of the bismuth on the market, in fact, is obtained as a by-product in the refining of other metals, such as lead, copper, and tin.

Production of Bismuth.—Native bismuth is separated from the gangue by heating the ore in cast-iron pipes set in the fire in an inclined position. The melted metal is collected as it drains from the lower end of the pipe.

Oxide ores are reduced with carbon in crucibles, or in small reverberatory furnaces, in the presence of a flux that will convert the gangue into a readily fusible slag. Metallic iron is employed in the charge to transpose the relatively small amount of bismuth sulfide that may be present into metallic bismuth and sulfide of iron. Sulfide ores are first roasted to the oxide and are then reduced in the same manner as the native oxides.

The crude bismuth is sometimes refined by heating at a carefully controlled temperature on a sloping iron hearth. The bismuth, having a low melting point, drains away. Melting in the presence of fluxes gives better results. A purer product is prepared by dissolving the crude bismuth in nitric acid, and then precipitating the basic nitrate with water, thus:



$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3$$

The insoluble basic nitrate is collected, dried, calcined to the oxide, and then is reduced with carbon.

Physical Properties.—Bismuth, like antimony, is hard, highly crystalline, and brittle. It may be distinguished from antimony by the fact that the crystals of bismuth have a reddish sheen. The density of solid bismuth is 9.82 and that of the liquid at the melting point is 10.05, so that on solidification there is an expansion of over 2 per cent. The properties of the metal are summarized in Table 38.

TABLE 38.—PROPERTIES OF BISMUTH

Melting point	271°C. (519.8°F.)
Boiling point	1420°C. (2556°F.)
Density	9.82 g. per cc.
Electrical resistivity	115 microhms
Thermal conductivity	0.0200 c.g.s.
Modulus of elasticity	4.6×10^6 psi

Chemical Properties.—By dry air at ordinary temperatures bismuth is practically unaffected; in moist air, it oxidizes slightly and becomes iridescent. When heated in air, it burns to the trioxide Bi_2O_3. At a red heat it decomposes steam with the liberation of hydrogen. It unites directly with the halogens. It dissolves tardily in hot hydrochloric acid, but hot sulfuric acid converts it readily into the sulfate $Bi_2(SO_4)_3$ with the evolution of sulfur dioxide. In nitric acid and in aqua regia it dissolves readily; the former produces the nitrate $Bi(NO_3)_3$, and the latter the trichloride $BiCl_3$.

Uses.—About 70 per cent of the bismuth produced goes into the preparation of low-melting-point alloys (page 257), of which there are in the main two varieties: those that contain bismuth, lead, and tin, and those that contain cadmium in addition to the preceding. The lowest melting alloy has the following composition: bismuth, 50 per cent, lead, 25 per cent, and tin and cadmium each 12.5 per cent. It melts at 55.5°C. By varying the composition, almost any desired melting point may be obtained. Fusible alloys of this sort are employed in making electric fuses, safety plugs in boilers, sprinkler heads in automatic sprinkling devices, connecting links to hold in place automatic fire doors, etc. Bismuth is used also in low-melting casting alloys that contain bismuth, lead, tin, and cadmium (page 257). A recent application is in Matrix Alloy for holding different parts of complex dies. These contain bismuth, lead, tin, and antimony.

Because of its expansion when solidifying, bismuth is useful in cast alloys that are required to take sharply the impressions

of the mold. It is less employed than antimony for this purpose, however, because bismuth is more costly.

ANTIMONY

Ores and Occurrence.—Occasionally, in small quantities, antimony is found free in nature, but the chief ore is *stibnite*, the black trisulfide, Sb_2S_3, of which a plentiful supply is found in China and notable quantities in Bolivia, Mexico, Algeria, and Czechoslovakia. China formerly contributed approximately 90 per cent of the world's total output of antimony, and about 95 per cent of the production came from the province of Hunan, where the largest known deposits in the world occur. Because of low labor charges and its large deposits of ore, China dominated the world's antimony market. Today, Mexico is an important source, supplying this country with 57 per cent of our total imports. The world's production of antimony is about 38,000 tons annually, about half of which is consumed in the United States.

Metallurgy.—There are several methods for extracting antimony from its ores. In China the usual process consists of roasting the stibnite to the oxide, and then reducing the oxide with carbon. In other countries the trisulfide is heated with scrap iron which separates metallic antimony, as follows:



$$Sb_2S_3 + 3Fe = 2Sb + 3FeS$$

To a small extent, antimony is obtained as a by-product in the refining of other metals, such as lead, copper, zinc, and silver.

Properties.—Antimony is silvery white, hard, highly crystalline, and so brittle that it may be readily powdered under the hammer. At ordinary temperatures antimony is chemically stable and does not tarnish in air, but when heated it burns with a bluish flame, forming the white, powdery antimony trioxide, Sb_2O_3.

In cold, dilute sulfuric acid, antimony is unaffected, but it dissolves in the hot concentrated acid. If finely divided, it is attacked

TABLE 39.—PROPERTIES OF ANTIMONY

Melting point	630°C. (1166°F.)
Boiling point	1140°C. (2624°F.)
Density	6.62 g. per cc.
Electrical resistivity	39 microhms
Thermal conductivity	0.044 c.g.s.
Modulus of elasticity	11.3×10^6 psi

by hydrochloric acid. Concentrated nitric acid converts it into the trioxide. In aqua regia it dissolves readily with the formation of the pentachloride.

The properties of antimony are summarized in Table 39.

Uses.—Antimony readily forms alloys with most of the heavy metals; in its metallic form it has few other uses. Hardness is its chief contribution to such alloys in most cases, but because it considerably increases the fluidity, advantage is taken of this property in preparing alloys to be cast with sharp detail, especially in type alloys. The metals with which antimony is most commonly alloyed are lead, tin, and copper.

About 90 per cent of the antimony consumed in the United States is employed for the following uses, which are named in the order of decreasing magnitude of consumption: Babbitt alloy (page 249), storage-battery plates, soft metal alloys and solder, hard lead (for pipes, traps, etc.), type alloys, for vulcanizing rubber (in the form of the pentasulfide), bearing alloys, as oxide and sulfide in enamels for metalware, and in cable coverings. The antimony employed in storage-battery plates serves to make them more rigid and less likely to buckle. About 90 per cent of the antimony employed for this purpose is recovered.

Antimony is an important war metal. It is employed for hardening shrapnel bullets, in primers, and to produce white smoke for range finding. Antimony is a component of many low-melting-point alloys (page 257), such as fuse blocks for indicating heated bearings.

Mercury

Occurrence.—The largest mercury mine in the world is in Spain, the government-owned Almaden mine in the province of Ciudad Real. In Italy are several important mines, government owned in one district, the combined output of which in some years exceeds that of the Almaden. Regardless of which surpasses the other, these two countries together supply approximately 90 per cent of the world's total annual production of 3,500 to 4,000 metric tons of the metal.[1] In mercury output, the United States ranks third and Mexico fourth. California and Oregon are the chief producers in the United States, but in this country the imports of mercury are about twice as great as the domestic production.

[1] It is the custom to market mercury in iron flasks of 75 lb. capacity tightly closed with a threaded cover.

Occasionally mercury is found free and in amalgams of gold and silver, but most of the world's supply is obtained from *cinnabar*, the red sulfide, HgS.

Production.—Mercury is extracted from cinnabar by roasting the ore in the presence of air, usually in some type of shaft furnace. The fuel, charcoal or coke, is charged with the ore. The sulfur is oxidized and the mercury is set free in accordance with the following equation:



$$HgS + O_2 = Hg + SO_2$$

At the temperature of the reaction zone, any mercuric oxide produced would instantly be decomposed. The free mercury, vaporizing, passes from the furnace with the products of combustion and is recovered in a condensing system made up of brick chambers and long strings of tile pipe. Periodically the condensers are cleaned and the mercury is separated from the dust and soot by pressing it through linen or chamois skin. The metal may be purified by washing with nitric acid or by redistillation in the presence of air, which causes the vapors of volatile base metals, such as zinc and cadmium, to be converted into their oxides.

Properties.—Mercury is the only common metal that is liquid at ordinary temperatures, its freezing point being at −38.9°C. The boiling point of the metal is also low (357°C.), so that it has a noticeable vapor pressure even at ordinary temperatures. When gold leaf is suspended above the metal, its surface becomes coated with mercury in time. In the liquid and solid forms, mercury is an excellent conductor of electricity. The vapor is not conductive in the cold, but once an arc is struck, the current flows readily, producing the characteristic mercury spectrum, rich in green and ultraviolet rays. Mercury-vapor arc lights, among other uses, are employed in photographic work, in sterilizing water, and in connection with neon lights in the construction of illuminated signs.

Except in the presence of hydrogen sulfide, mercury is not affected by exposure to air at ordinary temperatures. When heated in air to about 300°C., it combines slowly with oxygen to form the red oxide HgO; when heated to a still higher temperature, the oxide that has been formed decomposes.

In hydrochloric and cold sulfuric acids, mercury is practically unaffected, but it dissolves in hot concentrated sulfuric and cold nitric acids. The alkaline hydroxides are without action upon it. The alloys of mercury are known as *amalgams*. All metals except

iron and platinum form amalgams, and even platinum will amalgamate under certain conditions.

The properties of mercury are summarized in Table 40.

TABLE 40.—PROPERTIES OF MERCURY

Melting point	−38.9°C. (−28°F.)
Boiling point	357°C. (674.6°F.)
Density (20°C.)	13.546 g. per cc.
Electrical resistivity	95.8 microhms
Thermal conductivity	0.0200 c.g.s.

Uses.—Most of the mercury consumed in this country finds outlet in the form of mercury compounds. One of the largest uses is for the manufacture of mercuric fulminate, $Hg(OCN)_2$, employed for blasting caps and other detonators because under percussion it explodes. In the form of the artificial sulfide, mercury is used in coloring red rubber products. Antifouling paints for ship bottoms are made with the aid of the red oxide of mercury, which the salt of the sea slowly converts into mercuric chloride, an active poison. Only a comparatively small amount of the metal is needed for thermometers, barometers, air pumps, and other laboratory apparatus and scientific instruments.

Recently in the electric-light plant of Hartford, Conn., mercury vapor, generated in a mercury boiler, has been employed effectively to operate the turbine of a prime mover for developing electric power. The original installation, generating 5,000 hp., required 2,800 lb. of mercury, but after about four years of operation an order was placed for additional equipment including a 10,000-kw., mercury-vapor turbine requiring about 13 lb. of mercury per kilowatt of capacity.[1] The mercury, of course, is employed in a closed system. Steam for an auxiliary unit is generated by the heat still resident in the mercury vapor after it passes the turbines.[2]

TITANIUM

Occurrence.—Titanium occurs in the earth more commonly than may be supposed. Among the elements it ranks tenth in order of abundance. The black, iron-bearing *ilmenite*, $FeTiO_3$, is the chief commercial source of titanium, but *rutile*, the dioxide TiO_2, also is frequently found. Other mineral forms of the dioxide are known

[1] FURNESS, "Mineral Resources of the United States," Part I, p. 52, U.S. Geological Survey, 1927.

[2] For advantages of the mercury-vapor turbine over the steam turbine, see *Chem. Age.* (*N.Y.*), Feb. 19, 1927, p. 183.

as *brookite* and *anatase*. Workable deposits of both ilmenite and rutile, especially the former, occur in many parts of the world. The annual production of ilmenite in all countries combined is now probably in excess of 225,000 metric tons, with an estimated content of titanium dioxide ranging from 35 to 55 per cent. The chief contributors are the United States, Senegal, India, Norway, Brazil, Russia, and Canada. The domestic production is supplied chiefly by Virginia and Florida.

Metallic Titanium.—Because of the readiness with which titanium forms carbides, nitrides, and silicides at high temperature, it is difficult to prepare the metal in a free state. It is possible to reduce the oxide by means of aluminum, a little of which enters into an alloy with the titanium. Like many other metals, titanium is steel gray in color. It is comparatively hard, but is sufficiently malleable to be worked at a red heat. It has a density of 4.5 and melts *in vacuo* at 1800°C. (3272°F.).

When titanium is heated in the air, it burns with a very brilliant incandescence; the dioxide is formed. It is one of the few metals that combine directly with nitrogen when heated in it. It decomposes boiling water with the evolution of hydrogen, and it dissolves in hydrochloric and sulfuric acids in the usual manner.

Industrial Application.—When industrial applications of titanium were first made, it was used in the form of ferrotitanium as a deoxidizing agent in the manufacture of steel; now attention is directed chiefly to its employment in the form of the dioxide as a white pigment (page 551). Because the pigment is chemically very inert, in addition to its use in paints, lacquers, and enamels, it is employed in printing ink, rubber, oil cloth, linoleum, wall paper, window shades, etc.

Gold

Occurrence and Metallurgy.—Gold is one of the few metals that occur principally in the native state. It is found in veins in quartz rock, and in river sand and gravel, usually alloyed with copper and silver. It occurs also in small amounts in ores in combination with tellurium or with tellurium and silver. A considerable amount of gold is obtained as a by-product from the refining of copper, lead, and nickel.

The oldest method of recovering gold depends on its high density. The lighter sands and gravel can be washed away by panning, sluicing, or by more elaborate hydraulic methods. The impure

gold thus obtained is separated from copper and silver by treatment with sulfuric or nitric acid in which gold is insoluble. For extraction from low-grade ores two processes are in use. The *amalgamation process* treats the finely ground ore with mercury, in which gold is readily soluble. The mercury is then distilled off and recovered, leaving the gold as a residue. The *cyanide process* depends on the fact that metallic gold is soluble in potassium cyanide in the presence of oxygen, according to the reaction:



$$2Au + 4KCN + \frac{1}{2}O_2 + H_2O = 2KAu(CN)_2 + 2KOH$$

The soluble potassium aurous cyanide, $KAu(CN)_2$, is treated with metallic zinc or aluminum which reduces the gold to the metallic state. Another method of recovery is by electrolysis of this solution.

The world production of gold in 1937 amounted to 34,635,000 oz., of which about 4,000,000 oz. were produced in the United States.

Physical Properties.—Gold is an extremely soft metal. It is extraordinarily malleable and ductile, and, next to silver and copper, is the best conductor of electricity. It offers remarkable resistance to atmospheric corrosion and tarnish. The properties of gold are summarized in Table 41.

TABLE 41.—PROPERTIES OF GOLD

Melting point	1063°C. (1913°F.)
Boiling point	2966°C. (5339°F.)
Density	19.3 g. per cc.
Electrical resistivity	2.42 microhms
Thermal conductivity	0.7072 c.g.s.
Tensile strength	20,000 psi, cast
	37,000 psi, hard-drawn wire
Modulus of elasticity	11.3×10^6 psi

Uses.—Since it occurs in the native state, gold was one of the earliest metals discovered and used by man. Because of its scarcity, its unusual and beautiful color, and its resistance to corrosion and even fire, it was prized for decorative purposes and even became an object of worship in some early civilizations. In fact a residue of this glorification of gold persists today in its adoption as an almost universal monetary standard. However, outside of this somewhat artificial function, it is one of the most useless of the well-known metals. It is much too soft for use as coinage or jewelry, so that all gold used for these purposes contains silver or copper, or both,

as alloying elements to increase the hardness. The various proportions of these alloying elements give a series of colors ranging from red through yellow to green. The gold content of coinage or jewelry may be expressed in terms of "fineness," which is the number of parts of gold per thousand parts by weight of the alloy. Jewelers express the gold content of their alloys in "carats," on which scale 24 carat (abbreviated 24 kt.) is pure gold, and the number of parts of gold, by weight, in 24 parts of alloy gives the carat directly. Thus 14 kt. gold contains 10 parts of base metal (copper, silver, nickel, etc.) to 14 parts of gold and is 58.33 per cent gold.

Beside the use in coinage and jewelry, an appreciable quantity of the metal is used in dentistry. It is the principal constituent of bridge alloys, which may contain in addition platinum, palladium, silver, and other metals. It is also used as sponge or foil in filling tooth cavities.

The use of gold as a protective coating on base metals is another important application. Electroplating is the most common method of applying this coating. The terms "gold filled" and "rolled gold" are used to designate articles made of base metal on which a layer of carat gold has been fixed by brazing or welding and then drawn or rolled to the desired dimension.

Silver

Occurrence and Metallurgy.—Silver, like gold, occurs in the native state, usually associated with native copper. It occurs also as the chloride, AgCl, in the mineral *cerargyrite*, or *horn silver*. Numerous more or less complex sulfide ores are also found. A considerable portion of silver is produced in the smelting and refining of lead and copper ores. The recovery of silver from its ores is carried out by the cyanide process which is identical with that used for the extraction of gold. If the ore is of the sulfide type, it is first converted to the chloride by roasting and heating with sodium chloride before extraction with cyanide.

In 1937 the world production of silver amounted to 278,927,000 oz., of which the United States produced 71,735,000 oz.

Properties.—Silver is the whitest of the metals. It is harder than copper, is malleable and ductile, and is the best conductor of heat and electricity. Its luster is retained indefinitely unless hydrogen sulfide is present in the air, when a superficial blackening occurs due to the formation of silver sulfide, Ag_2S. Silver does not dissolve in dilute hydrochloric or sulfuric acids, but dissolves

readily in nitric acid and in concentrated sulfuric acid. The properties of the metal are summarized in Table 42.

TABLE 42.—PROPERTIES OF SILVER

Melting point	961°C. (1730°F.)
Boiling point	2212°C. (3982°F.)
Density	10.5 g. per cc.
Electrical resistivity	1.62 microhms
Thermal conductivity	0.974 c.g.s.
Tensile strength	40,000 psi, cast
	51,000 psi, hard drawn
Modulus of elasticity	10.3×10^6 psi

Uses.—Silver, like gold, is extensively used for coinage, in which case various percentages of copper are added to increase the hardness. The silver content of coinage is stated in terms of fineness, as with gold, ranging in different countries from 500 to 900. The use of the metal in silverware and jewelry dates from earliest times, and the fineness varies from 750 to 950. Sterling silver, 925 fine, is the standard in this country.

Electroplating of silver as a protective coating on base metal, usually German silver (nickel, zinc, copper) (page 239), accounts for a large proportion of the total silver used. Another method of applying the coating is the bimetal-plate method similar to that used in preparing "gold-filled" (page 203) articles. The famous Sheffield plate was made by this method.

Considerable quantities of silver are used in special alloys in the electrical industries, in silver solders, dental alloys, in mirrors, and in the form of the halogen derivatives in photography. Small quantities of silver are used also in medicine, silver derivatives having powerful antiseptic properties.

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CHAPTER V

NONFERROUS ALLOYS

By Harry Seltz, Ph.D

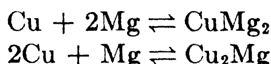
In the preceding chapter the industrially important metals were discussed. Were we limited to the use of those 30 or more metals in the pure state, the vast range of properties required by modern technology could not be met. It is possible, of course, to modify somewhat the mechanical properties of pure metals by cold work and by controlled annealing, but these effects are relatively minor. Fortunately, most diverse properties can be produced by the combination of two or more metals to form alloys. *An alloy may be defined as a coherent metallic mass produced by the intimate association of two or more metals.* In some cases also the introduction of nonmetals such as carbon, silicon, phosphorus, boron, sulfur, and even nitrogen or oxygen may produce marked effects. It is apparent that thousands of combinations resulting in useful alloys are possible.

Alloys are generally made by mixing the constituent metals in the liquid state and allowing the mass to cool. These systems are usually homogeneous solutions while molten, but on solidification they often form heterogeneous solids with two or more distinct and discrete "phases" appearing. To understand the relation between composition and properties and to understand the changes that occur during heat-treatment and hardening of alloys, it is necessary to study the nature of the phases that appear on solidification and to determine whether any fundamental laws govern their formation. A most important principle restricting the *number* of phases that can exist *in equilibrium* in a given system was deduced by the famous scientist, Willard Gibbs, and this principle has had a great influence on the development of modern metallurgy. It is embodied in a statement called the "phase rule," which Gibbs arrived at by rigorous thermodynamic reasoning, but which here can be considered only from an elementary standpoint. Use will be made of the phase rule in this chapter in discussing the equilibrium relations in several alloy systems.

The Phase Rule.—Before the phase rule is stated, three terms must be defined:

1. The *number of phases* in a system is the number of distinct and different homogeneous portions that go to make up the system. If liquid water is in equilibrium with water vapor, this system is made up of two phases. If ice, liquid water, and water vapor are in equilibrium, there are three phases. It should be stated that the degree of subdivision of a phase does not influence a condition of equilibrium unless the particles approach colloidal dimensions. In alloys it is often necessary to use high magnifications to detect the presence of the different solid phases.

2. The *number of components* of a system is the *smallest* number of substances required to define the composition of every phase of a system at equilibrium. In alloys this will be merely the number of elements of which the alloy is composed. In the copper-magnesium alloys, for example, at certain compositions the compounds $CuMg_2$ and Cu_2Mg appear as solid phases. These can be related to the pure metals by the equilibria:



$$Cu + 2Mg \rightleftharpoons CuMg_2$$
$$2Cu + Mg \rightleftharpoons Cu_2Mg$$

and hence are not considered as additional components since their concentrations can be fixed in terms of the concentrations of Cu and Mg and the equilibrium requirements for these reactions.

3. The *number of degrees of freedom* is the number of variables of the system which must be fixed to define the system completely. The variables that influence equilibrium are primarily pressure, temperature, and concentrations of the components in the several phases. The number of degrees of freedom can be defined also as the number of these variables that can be changed independently without causing the disappearance of one of the phases in equilibrium.

The phase rule relates the three quantities defined above by the simple equation:

$$P + F = C + 2$$

where P = number of phases.
C = number of components.
F = number of degrees of freedom.

This relationship is rigorously true for any system *at equilibrium*, and limits the number of phases that can exist in equilibrium under

any conditions. The *maximum* number of phases in a system of a given number of components will be the number given by the above equation when the number of degrees of freedom, F, is equal to zero. When a system is made up of a single pure substance and hence $C = 1$, then, when $F = 0$, it follows that $P = 3$. This means that for a pure substance the maximum number of phases that can exist in equilibrium is three, and this three-phase equilibrium can be established at one definite pressure and temperature, and the concentrations (densities) of the phases are completely fixed. A system showing zero degrees of freedom is said to be "invariant." The most common case of invariant equilibrium in a one-component system is that between solid, liquid, and vapor. Ice, liquid water, and water vapor can exist in equilibrium only at +0.0076°C., at a pressure of 4.6 mm.; the specific volume of the ice phase is 1.0914 cc. per g., of the liquid phase is 1.000132 cc. per g., and of the vapor phase is 210 liters per g. If then these phases are in equilibrium and an attempt is made to increase the temperature by supplying heat, or an attempt is made to increase the pressure by decreasing the volume, these attempts will fail until one or another phase has disappeared. As heat is added, for instance, ice will melt, taking up 80 cal. of heat for each gram melted, so that constant temperature is maintained until all of the ice has disappeared. The system then becomes two phase, liquid plus vapor, and according to the phase rule has one degree of freedom. The system is then said to be "univariant" and the two phases can be kept in equilibrium with any arbitrary change of temperature, within certain limits. However, as soon as the temperature is fixed at some definite value, there can be but one value of the pressure, the equilibrium vapor pressure. At 100°C., for example, liquid water and water vapor can exist in equilibrium only at a pressure of 1 atm.

Although these relations seem obvious for a one-component system, without the phase rule it would not be obvious that the maximum number of phases that can exist in equilibrium in a two-component system is four, in a three-component system is five, and so on.

In the phase rule as stated, the factor "2" really enters the equation as representing the two variables, temperature and pressure. In most metallurgical applications the pressure is fixed at atmospheric, a pressure too high for the existence of a vapor phase. In other words, one degree of freedom, the pressure, is already utilized, and furthermore, since any ordinary changes of pressure

have negligible effects on equilibria in condensed (no vapor phase) systems, the phase rule is simplified to the form:

$$P + F = C + 1$$

This would seem to be contradictory to the more general form of the phase rule, since it leads to the conclusion that *two* is the maximum number of phases ($F = 0$) in a one-component system, whereas actually three phases can exist in equilibrium. The point is, of course, that with fixed pressure the chance that this pressure would be precisely that required for a three-phase equilibrium is negligible. Similarly for a two-component condensed system, with fixed pressure, the maximum number of phases is three, for a three-component system is four, and so on. A two-component system in which a liquid and two solids are in equilibrium can be considered invariant even though a change of pressure would actually produce a slight but negligible change in the equilibrium temperature and composition, just as the freezing point of a pure liquid is insensibly affected by ordinary pressure changes. This simplified form of the phase rule will be used here in the discussion of alloy systems.

Types of Phase Equilibria in Alloy Systems

It is customary to refer to an alloy containing two components as a binary alloy, with three components as a ternary alloy, and so on. In binary metal systems, according to the phase rule, when two phases, such as a liquid and a solid, are in equilibrium, there is one degree of freedom:

$$\begin{aligned} 2 + F &= 2 + 1 \\ F &= 1 \end{aligned}$$

These two phases thus can exist in equilibrium over a definite temperature range. As soon as the temperature is fixed, however, the compositions of the liquid and solid phases in equilibrium are likewise fixed. It is, in general, difficult to calculate precisely these conditions of equilibrium, and experimental determination must be resorted to. Again, if three phases, such as a liquid and two solids, are in equilibrium, the system is invariant. These three phases can be in equilibrium at one temperature only, and the compositions of the phases are fixed. Any attempt to change the temperature or composition must result finally in the disappearance of at least one phase. The types of two- and three-phase equilibria that occur

in binary metal systems are limited and can be rather simply classified. Equilibria between liquid and solid phases can be divided into three classes: (1) the solid phases are the *pure metals;* (2) the solid phases are *intermetallic compounds* formed by a combination of integral numbers of atoms of the two metals, such as $CuMg_2$ and Cu_2Mg previously mentioned; (3) the solid phases are *solid solutions.* When a pure metal solidifies, the atoms are arranged on a space-lattice structure in a definite orderly manner, giving rise to a geometrical crystalline external form. When a solid solution of two metals appears, the second element usually replaces the atoms of the first element at random in its lattice structure. Such solid solutions are called *substitution* solid solutions, and certain distortion of the original lattice will occur. In some few instances the atoms of the second element, if they are small enough, may enter into the lattice to form *interstitial* solid solutions, occupying the empty spaces in the somewhat open structure of the lattice.

There are subdivisions to classifications (2) and (3), which will be considered in the following discussion of the three types.

Pure Metals as Solid Phases—Equilibrium Diagrams.—At the freezing point of a pure substance the solid and liquid phases are in equilibrium (page 124). If a second component is added to the liquid phase and if this component does not form a solid solution with the first, then the equilibrium or freezing point is always lowered. This is a familiar principle[1] and is well illustrated by the lowering of the freezing point of water by the addition of salts.

Exactly the same type of behavior is observed in some binary metal systems. Bismuth, melting at 271°C., and cadmium, melting at 321°C., are completely miscible in the liquid state. If a small amount of cadmium is added to liquid bismuth, the freezing point falls below 271°C. and, as additional cadmium is introduced, the equilibrium temperature is depressed still farther. Similarly, the addition of bismuth to liquid cadmium progressively lowers the freezing point to temperatures below 321°C. These "freezing point" curves are shown in Fig. 17 where it is seen that they finally intersect at 144°C., at a composition corresponding to 40 per cent of cadmium. At this point, called the *eutectic*, the liquid phase is in equilibrium simultaneously with solid bismuth and solid cadmium. This is a three-phase, invariant condition and, if heat is

[1] See McCutcheon, Seltz, and Warner, "General Chemistry," 3d ed., p. 181, D. Van Nostrand Company, Inc., New York (1939).

removed, the temperature remains constant while the phase change:



$$\text{Liquid (40 per cent Cd)} \rightleftharpoons \text{Cd}(s) + \text{Bi}(s)$$

takes place until all the liquid has disappeared. The entire liquid solidifies as a mixture of minute bismuth and cadmium crystals in a characteristic, laminated, *eutectic structure.* The individual crystals of the two metals in the eutectic solid can be observed only under the microscope. It is apparent that, for any composition, complete solidification will occur only when the eutectic temperature, 144°C., is reached. If a liquid containing 20 per cent of cadmium is slowly cooled, solid bismuth begins to separate at about

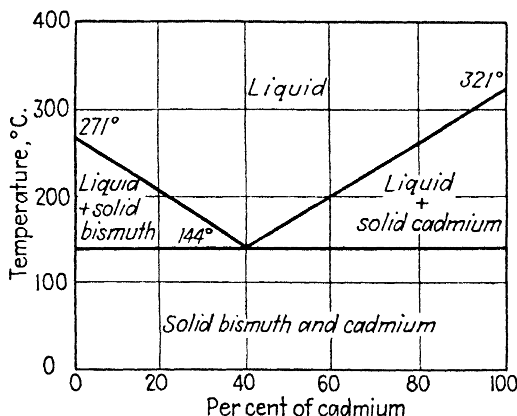


Fig. 17.—Equilibrium diagram for the bismuth-cadmium system.

210°C., as shown by the intersection of the 20 per cent composition line with the freezing-point curve. Below this point the system is univariant with the two phases, liquid and solid, in equilibrium. The solidification is accompanied by heat evolution and the cooling rate thus decreases. At the same time the liquid phase becomes richer in cadmium until the eutectic temperature and composition are reached. Here solid cadmium and bismuth separate simultaneously and the temperature remains constant until the mass has solidified completely.

On the other hand, if a liquid of the eutectic composition (40 per cent of cadmium) is cooled, no separation of solid occurs until the temperature reaches 144°C., when complete solidification occurs at constant temperature as in the freezing of a pure substance, and the solid alloy will show eutectic structure throughout.

On the cadmium side of the eutectic, pure solid cadmium separates down to the eutectic temperature, when again complete solidification follows. Cooling curves for pure bismuth and cadmium and for 20 per cent, 40 per cent, and 60 per cent of cadmium are shown in Fig. 18. In establishing these *cooling curves*, the temperature of the system is followed with a thermocouple at definite time intervals. The first breaks in the curves for 20 and 60 per cent of cadmium indicate the location of the freezing-point curve for these compositions. It will be noted that there is some supercooling before the first separation of the respective solids occurs. Then the cooling continues at a slower rate (owing to the heat evolution) down to the eutectic, when there is a complete tempera-

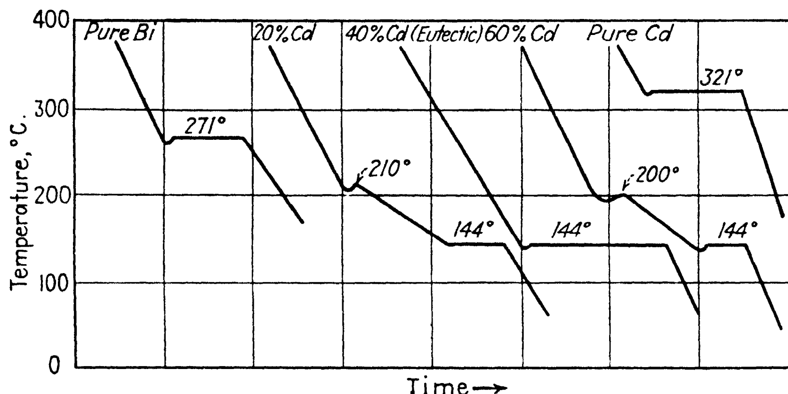


Fig. 18.—Cooling curves for the bismuth-cadmium system.

ture "arrest" during the final solidification. For the eutectic composition the cooling curve is similar to those of the pure substances. By taking a sufficient number of cooling curves at various compositions, the complete equilibrium diagram, shown in Fig. 17, can be constructed. A diagram, such as this, which shows the equilibrium relations at various compositions and temperatures, is called a *phase equilibrium diagram.*

Formation of Intermetallic Compounds.—The formation of intermetallic compounds gives rise to two types of equilibrium diagrams. In one the compound is stable up to its melting point where it can exist in equilibrium with a liquid of the same composition as the solid. This behavior is illustrated by the calcium-magnesium system (Fig. 19), in which the intermetallic compound Ca_3Mg_4 appears, melting at 720°C. As shown in the diagram, there are three two-phase regions, giving rise to two eutectics. Any composition from

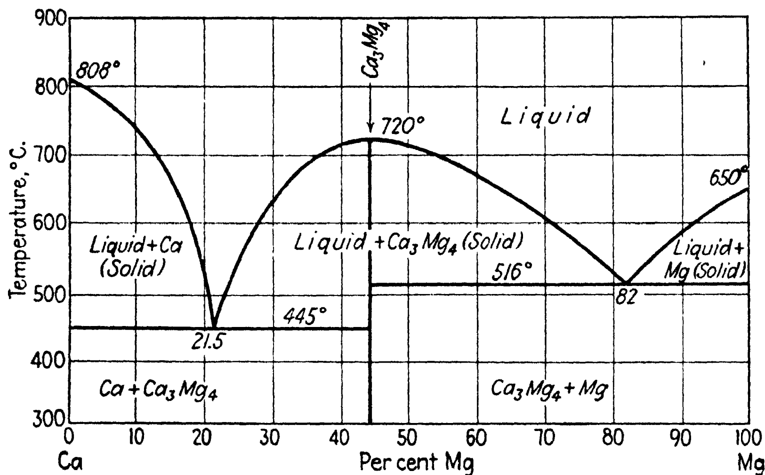


FIG. 19.—Equilibrium diagram for the calcium-magnesium system.

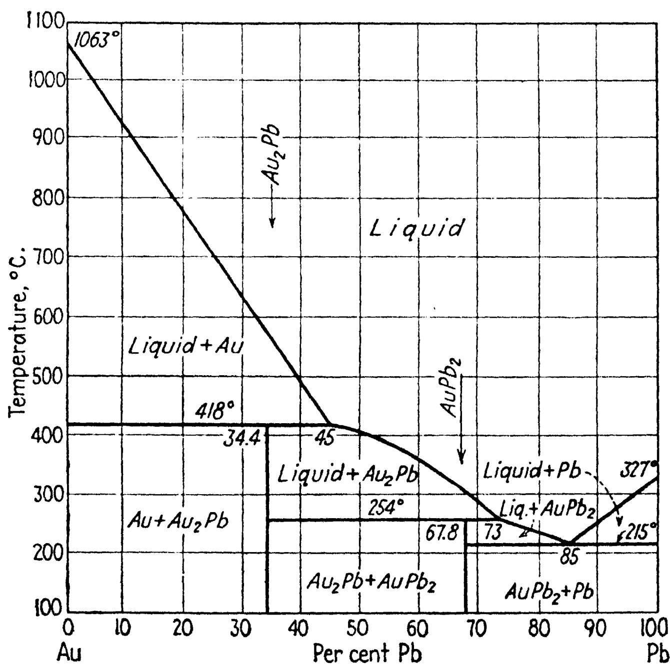


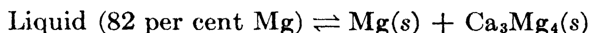
FIG. 20.—Equilibrium diagram for the gold-lead system.

0 to 44 per cent Mg solidifies completely at 445°C. where the eutectic liquid (21.5 per cent of Mg) separates solid calcium and solid Ca_3Mg_4:



$$\text{Liquid (21.5 per cent Mg)} \rightleftharpoons \text{Cd}(s) + \text{Ca}_3\text{Mg}_4(s)$$

Any composition from 44 to 100 per cent Mg solidifies completely at 516°C. in the eutectic reaction:



$$\text{Liquid (82 per cent Mg)} \rightleftharpoons \text{Mg}(s) + \text{Ca}_3\text{Mg}_4(s)$$

In other cases intermetallic compounds are not stable up to their melting points but decompose at lower temperatures to give a

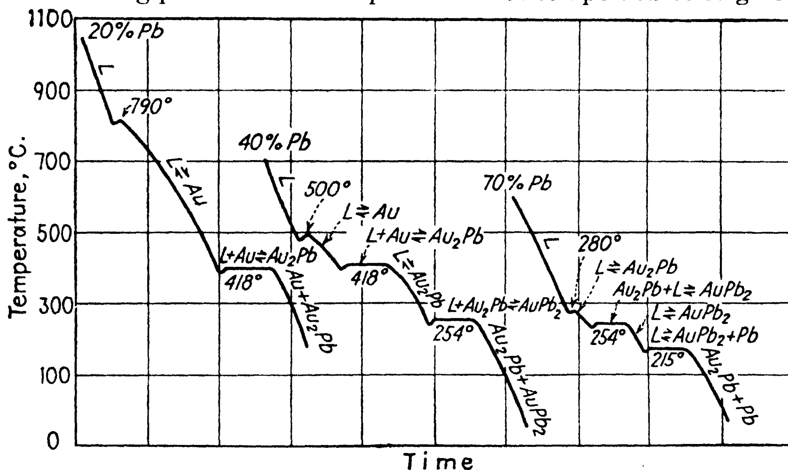
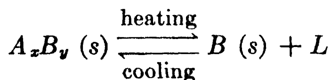


FIG. 21.—Cooling curves for the gold-lead system.

liquid, of composition different from that of the compound, and another solid, which may be one of the pure components. This is a three-phase invariant system and the compound disappears at constant temperature. On cooling, the opposite phase change takes place. This type of invariant behavior is called a *transition* or *peritectic* and can be generalized by the equilibrium



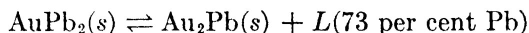
$$A_xB_y\ (s) \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} B\ (s) + L$$

where A_xB_y is the intermetallic compound, B is a solid component (or another compound), and L is the peritectic liquid of fixed composition. The gold-lead system (Fig. 20) is an example of this behavior, except that two compounds both showing transitions are found. At 418°C. the invariant transition:



$$Au_2Pb(s) \rightleftharpoons Au(s) + L(45 \text{ per cent Pb})$$

occurs. At 254°C. a second transition, involving the two compounds, is found:



$$AuPb_2(s) \rightleftharpoons Au_2Pb(s) + L(73 \text{ per cent Pb})$$

Cooling curves for 20, 40, and 70 per cent Pb alloys are shown in Fig. 21. It is apparent that for both types of systems a sufficient number of cooling curves would make it possible to construct the complete equilibrium diagrams.

Alloys containing a large proportion of intermetallic compounds as separate phases are not often of technical importance, since such compounds are usually hard and brittle with low strength and little ductility.

Solid Solution Formation.—There are three fundamental types of equilibrium diagrams resulting from the formation of solid solutions. A solid solution has been defined as a homogeneous crystalline mixture of two or more metals. If the space-lattices of the two pure metals are of the same kind, both face-centered cubic, for example, and the dimensions of the two are not very different, then it is possible for these elements to form a continuous series of solid solutions over the entire range of composition from 100 per cent of one to 100 per cent of the other, just as alcohol and water are miscible in all proportions in the liquid state. In the other two types the metals show limited solid solubility.

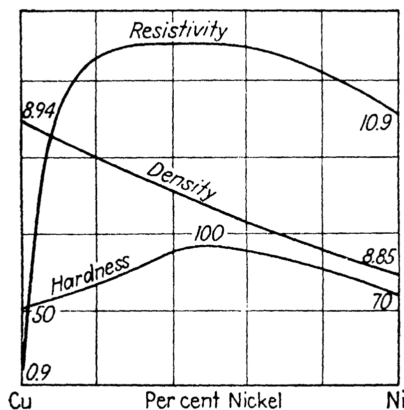


FIG. 22.—Electrical resistivity, density, and hardness of copper-nickel solid solutions.

Equilibrium Diagrams for Complete Solid Miscibility.—Copper and nickel both crystallize in the cubic system with face-centered lattices, and the unit cube for copper is 3.608 Å.[1] and for nickel is 3.517 Å. It thus is possible to substitute nickel atoms at random in the copper lattice without discontinuity until the crystal is 100 per cent nickel. The properties of these solid solutions, such as

[1] One angstrom unit (Å.) = 10^{-8} cm.

density, tensile strength, and electrical resistivity, change continuously from those of pure copper to those of pure nickel (Fig. 22).

The equilibrium diagram for such a system is very simple. The maximum number of phases in equilibrium cannot exceed two, one liquid and one solid solution, and no invariant condition appears. If nickel is added to molten copper and the temperature is slowly decreased, a solid phase will appear at a temperature *above* the freezing point of pure copper. The freezing point, instead of being lowered, is raised, because the solid solution that separates contains a higher percentage of nickel than the liquid from which it is formed. As more and more nickel is added, the freezing point increases

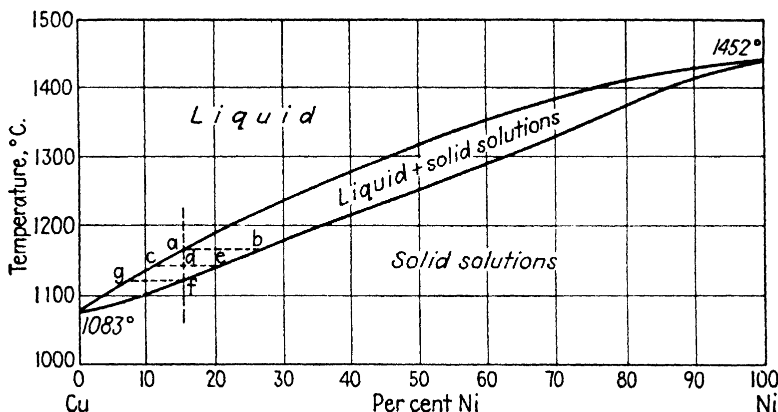


Fig. 23.—Equilibrium diagram for the copper-nickel system.

toward that of pure nickel. The equilibrium diagram is shown in Fig. 23, where the upper curve called the *liquidus* gives the freezing point for each composition, and the lower curve called the *solidus* shows the composition of the solid in equilibrium with the liquid at any temperature. The behavior of a liquid of the composition represented by the dotted line on cooling from a temperature above the liquidus is as follows: As the temperature reaches the point *a* a solid of composition *b* first begins to separate; and the rate of cooling decreases due to the heat evolved in the solidification. The isothermal line *ab*, called a *tie line*, joins the two phases in equilibrium. The system is now two phase and hence univariant; the temperature can be lowered but at each new temperature the composition of liquid and solid solutions in equilibrium must correspond to those given by the tie line. At the temperature *d* the liquid has the composition, *c*, and the solid, *e*. At this point the amount of

liquid remaining is the fraction *de*/*ce* of the original, and the fraction *cd*/*ce* has solidified. At the temperature *f* the last trace of liquid of composition *g* disappears giving a homogeneous solid solution of the same composition as the original liquid, if *equilibrium has been maintained over the solidification interval.* In the process

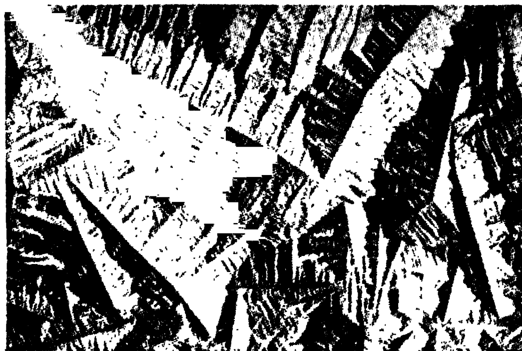


FIG. 24.—Dendrites in antimony. (*Howe.*)



FIG. 25.—Rapidly cooled 88 per cent copper, 10 per cent tin, and 2 per cent zinc alloy, showing coring. 140 diameters. (*Courtesy of Metals Research Laboratory, Carnegie Institute of Technology.*)

of solidification the crystals tend to form in the same manner as they do in pure metals. A central trunk develops, and parallel branches grow out from its sides, as illustrated in Fig. 24 for pure antimony. However, in the formation of a solid solution, a continuous change in composition of the solid takes place as it increases in amount.

This involves a process of diffusion in the solid that is relatively slow. If the alloy is cooled too rapidly, the liquidus-solidus range equilibrium will not be maintained. When the main trunk and branches of the dendrite first form, they will be richer in the higher melting component and a "cored" crystal will be produced by adding layers increasingly rich in the lower melting component as shown in Fig. 25. The alloy may be homogenized by heating for an extended period below the solidus temperature, where diffusion in the solid may eventually produce the uniform equilibrium composition with complete disappearance of the original dendrites, as shown in Fig. 26 for a copper-nickel alloy.

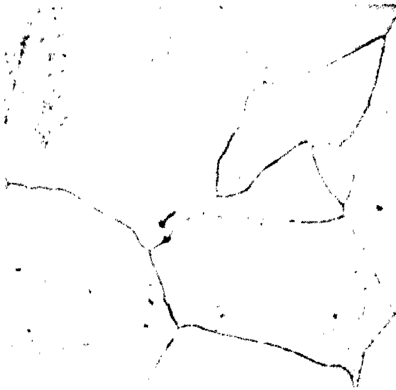


FIG. 26.—Copper-nickel alloy, containing 30 per cent of nickel, annealed, etched with acid ferric chloride. Uniform solid solution. 60 diameters. (*Kurnakow and Zemczuzny.*)

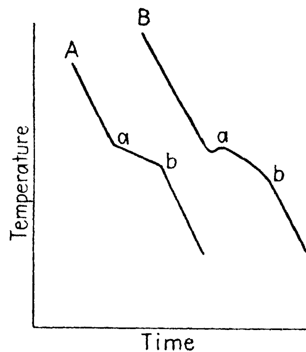


FIG. 27.—Ideal (*A*) and experimental (*B*) cooling curves for solid-solution formation.

The experimental determination of the liquidus line in Fig. 23 can be made from cooling curves, but the solidus is not readily fixed by this method as shown by typical cooling curves (Fig. 27) in a system of this kind. *A* represents an ideal curve, where the region from *a* to *b* is that of the two-phase liquid-solid equilibrium, the point *a* fixing the liquidus line and *b* the solidus line. *B* is an actual cooling curve, where the liquidus temperature is still apparent at *a* but, due to the difficulty in maintaining equilibrium, the solidus temperature in the neighborhood of *b* is not sharply defined.

In the copper-nickel system it should be noted that the freezing point of copper is *raised* and that the freezing point of nickel is *lowered* by the addition of the other component. In some systems showing complete solid solubility both components show a decrease

of freezing point on the addition of the other metal. Since the liquidus and solidus curves must be continuous, a minimum occurs at which the two curves coincide, as shown in Fig. 28 for the gold-copper system.

Another possibility is that both freezing points might be raised, giving rise to a diagram illustrated by Fig. 29. No metal systems have been found showing such behavior.

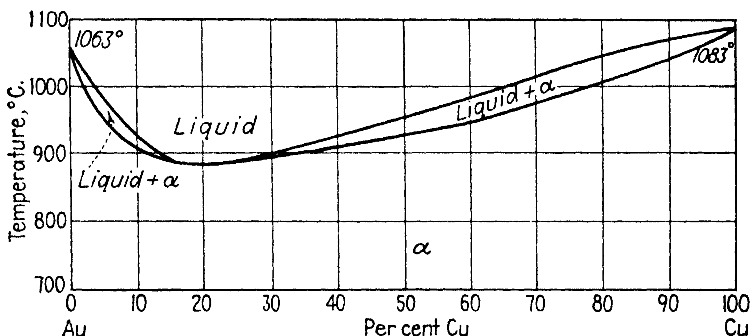


FIG. 28.—Equilibrium diagram for the gold-copper system.

Partial Miscibility in the Solid State.—In many metal systems the amount of a second metal that can be substituted in the lattice of another metal is limited. At a given temperature a certain *maximum solid solubility* exists. An attempt to introduce a greater amount of the second element results in the appearance of another solid phase, which may have the lattice structure of this second element with a saturation amount of the first in a substitutional type of solid solution. Since the appearance of this second phase makes the system univariant, at a given temperature the composition of the two equilibrium solids must be fixed. In most cases the equilibrium solid solubilities increase with higher temperatures.

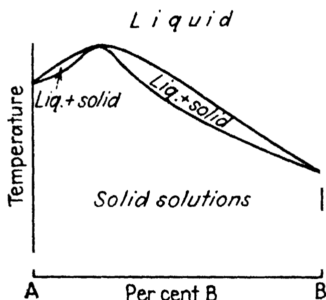


FIG. 29.—Equilibrium diagram for a continuous series of solid solutions with a maximum.

The occurrence of such equilibrium solid solutions, usually designated by the Greek letters α and β, gives rise to two types of equilibrium diagrams. If the freezing point of each metal is lowered by the addition of the other, the phase diagram will have the appearance shown by the lead-antimony system (Fig. 30). At 247°C. the

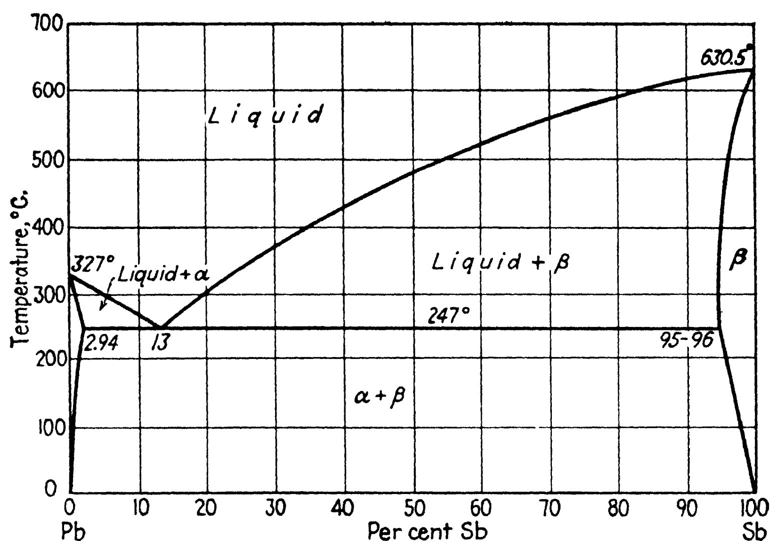


FIG. 30.—Equilibrium diagram for the lead-antimony system.

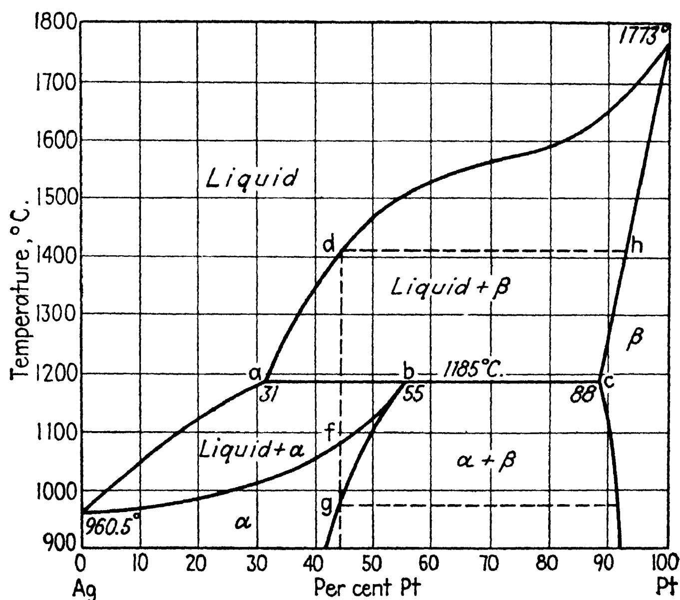
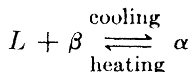


FIG. 31.—Equilibrium diagram for the silver-platinum system.

liquidus curves for the α and β solid solutions intersect at a composition of 13 per cent of antimony. This liquid then is in equilibrium with an α solid solution of lead containing 2.94 per cent of antimony and also with a β solid solution of antimony containing about 5 per cent of lead. This is an invariant eutectic equilibrium similar to that in the cadmium-bismuth system, except that here the solid phases are not the pure components. Below the eutectic temperature the two-phase $\alpha + \beta$ equilibrium shows decreasing solid solubility with decreasing temperature until at room temperature only a very slight solid solubility persists.

If, with partial solid solubility, one component shows a rise in freezing point and the other shows a lowering, an invariant three-phase equilibrium occurs of a peritectic type instead of a eutectic. This is illustrated by the silver-platinum diagram (Fig. 31). Here the liquidus curves for the α and β solid solutions intersect at 1185°C. at 31 per cent of platinum, which is a composition richer in silver than both equilibrium solids. The invariant phase change thus becomes:



$$L + \beta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha$$

and the final solid phases at various compositions are apparent from the diagram. It is instructive to analyze the changes that occur on cooling a mixture of the composition indicated by the dotted line. Above d the system is completely liquid. At d a β solid solution of composition h separates and when the temperature reaches 1185°C. the liquid has the peritectic composition at a, and the equilibrium β solid solution has the composition c. At this temperature α solid solution of composition b appears and, as heat is removed, the peritectic phase change occurs until all of the initially separated β disappears. This leaves liquid and α in equilibrium until at the point f the system is completely solidified as homogeneous α solid solution. Further cooling to the point g brings the system into the two-phase, $\alpha + \beta$ region and β solid solutions should separate. However this phase reaction involves only solids and may be very slow. Such solid phase reactions are important in explaining the effect of heat-treatment and the hardening of alloys, and will be considered later.

Solid Phase Equilibria.—The fundamental types of liquid-solid equilibria have been discussed and a number of binary metal systems belong to one or another of these types. However, many systems

are made much more involved by showing combinations of two or more of these. In addition, further complications are introduced by the fact that more than one region of two-phase solid solution equilibria may exist in the same system. In the lead-antimony and silver-platinum diagrams only two solid solutions appear with the lattice structures of the pure metals. In addition to such *terminal solid solutions* some systems show *intermediate solid solutions* with structures different from those of the components. One, two, or more such intermediate solid phases may appear giving rise to two, three, or more two-phase solid regions, as indicated by Fig. 32. Here the terminal solid solutions are designated as α and γ and the

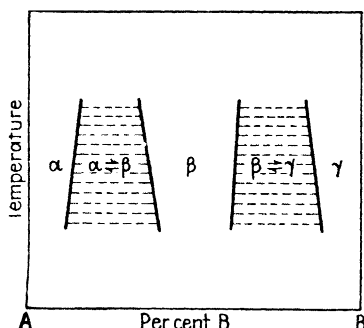


FIG. 32.—Intermediate solid solution with two two-phase regions.

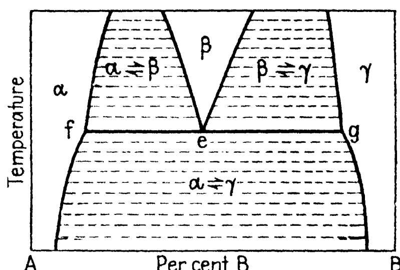
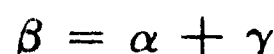


FIG. 33.—Intermediate solid solution with eutectoid.

intermediate by β, and the two-phase regions show the $\alpha \rightleftharpoons \beta$ and $\beta \rightleftharpoons \gamma$ equilibria. This may even result in an invariant equilibrium between three solids if the regions of immiscibility widen at lower temperatures as shown in Fig. 33. At e the β solid solution is in equilibrium with α of composition f and γ of composition g, and removal of heat should result in the isothermal phase change:



$$\beta = \alpha + \gamma$$

with complete disappearance of β. Because of the similarity of this reaction to that of a eutectic, it is called a *eutectoid phase change* and the mixture of α and γ formed by the decomposition of β may have a lamellar structure resembling that produced at a eutectic. However, we are dealing here with a complicated diffusion process in the solid state and in some cases it is possible to retain β solid solutions in a metastable state at temperatures below the eutectoid, by rapid cooling or quenching from higher temperatures. This metastable β, on the other hand, if reheated to temperatures just

below the eutectoid may undergo the normal phase change, resulting in increased hardness or some other change in mechanical properties. It can be seen that such solid phase reactions may permit of various *heat-treatments* to produce desired results.

In the remainder of this chapter and in the chapters on ferrous alloys the ideas developed here will be applied to several binary systems of great technical importance. Many alloys used today contain more than two components, but frequently the third or fourth components are present in relatively small amounts. It is beyond the scope of this book to enter into a discussion of ternary systems, and the student is referred to more specialized texts for further treatment of the phase rule.[1]

Crystallization, Deformation, and Annealing of Alloys

Before discussing particular alloys there are some general concepts of a physical nature that should be considered. These have to do with the size of grains (page 127) in metals and with the effect of mechanical distortion on these grains.

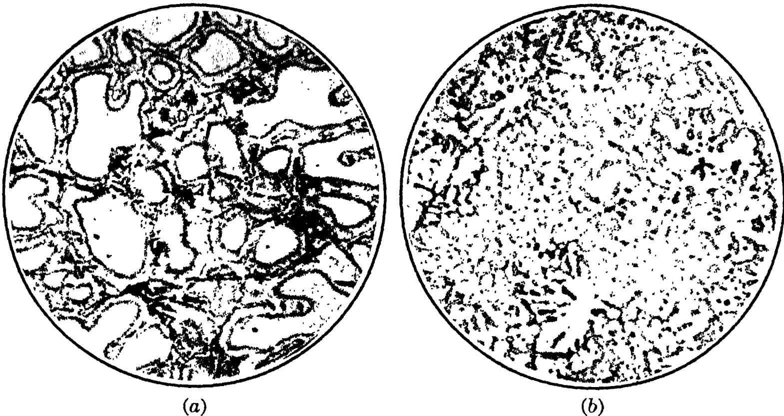
Crystal Size in Pure Metals and Alloys.—The rate of solidification and cooling of metals is the chief factor in determining the size of crystals in castings. The more slowly the crystals are formed, the larger they become, as shown in Figs. 34 and 35. Slow cooling allows a larger crystal growth (Figs. 34*a* and 35*a*), when the cooling has been sufficiently prolonged to allow the crystals that were first formed to float in that which was still melted. Large crystals are not usually desirable because they produce a weak alloy. Rapid cooling produces fine crystals, and makes a harder, stronger, and more uniform alloy, although one that is much more brittle and less ductile. The center of a mass of alloy, cooling more slowly, will consist of coarser crystals than the outside. It should be noted also that crystal growth does not cease with the solidification of the alloy. While still hot, the atoms have considerable freedom and can redistribute themselves. Then the larger crystals grow by absorbing the smaller ones.

The temperature at which the metal is poured has an effect on crystal size. With higher pouring temperatures, the mold becomes

[1] Findlay, "The Phase Rule," Longmans, Green and Company, New York (1920). Rivett, "The Phase Rule," Oxford University Press, New York (1923). Masing, "Ternäre Systeme," Akademische Verlagsgesellschaft m.b.H., Leipzig (1933).

more thoroughly heated. As a result, the cooling of the casting to the point below which crystal growth ceases is deferred.

Cold Working of Metals.—When metals are worked cold, they gain in hardness and strength but lose in ductility and shock resistance. In cold rolling and cold drawing, the crystals of the metal assume more or less the form of elongated platelets. If a suitably prepared specimen of metal that has been distorted in this manner is examined under the microscope, it will be found that the crystals show parallel lines running through them, changing direction from grain to grain. These lines are caused by a mass movement of crystal parts such as might appear when a stack of cards is pushed sidewise. The planes where the movement occurs are called



(*a*) (*b*)

Fig. 34.—Aluminum-copper alloy (8 per cent copper). (*a*) slowly cooled, (*b*) rapidly cooled. 100 diameters.

slip planes. Wire drawing is possible, then, because of the extension of crystals along slip planes. The slipping occurs through the crystals, not between them. If distortion of the metal is carried beyond that which can be accommodated by the slip planes, rupture occurs.

Cause of Hardening by Cold Work.—In his discussion of this topic, Campbell calls attention to the well-known fact that a piece of soft wire, such as annealed copper or low-carbon steel, may easily be bent with the fingers into the form of a hairpin, but that it is comparatively hard work to straighten it out again. Evidently the bending has produced some structural change in the metal that has increased its rigidity, an effect that is typical of all cold-working processes. Under the previous topic it was explained that the

permanent deformation produced by cold work is due to a block movement or shearing of crystals at planes of easy slip, called slip



FIG. 35a.—Alloy containing 79.7 per cent of lead, 14.5 per cent of antimony, and 5.8 per cent of tin slowly cooled, etched with nitric acid. The white crystals of antimony-tin solution have floated to the top of the ingot. 100 diameters. (*Gulliver.*)

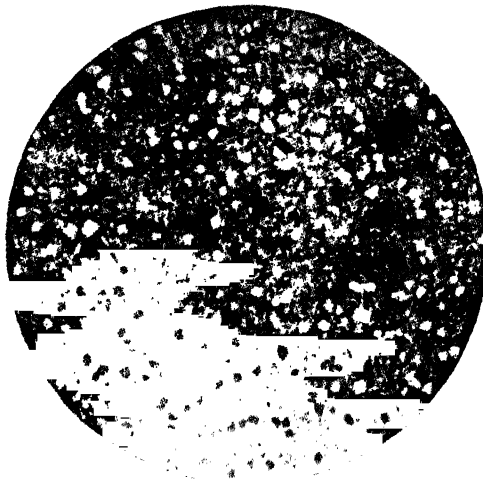


FIG. 35b.—Same alloy as that of Fig. 12. Quickly cooled, etched with nitric acid. The crystals are much smaller and are distributed with fair uniformity. 100 diameters. (*Gulliver.*)

planes. Any factor that interferes with this slip will harden and strengthen the metal. It is unquestionably true that part of this is

due to end resistance brought about by the obstruction of neighboring grains in which slip occurs in other directions. However, it has been found that, even with *single crystals*, increase of hardness occurs with deformation. Metallurgists today are inclined to attribute this to an actual distortion of the metal lattice itself, a conclusion that is supported by X-ray studies.

Annealing.—After cold working, as long as the temperature remains below a given point, which is different with different metals, the grains or crystals remain deformed; when heated to a



FIG. 36.—Rolled aluminum bronze containing 7.5 per cent of aluminum. 10 diameters. (*Law.*)

suitable temperature, known as the annealing temperature, they regain their symmetry and become equiaxed, as it is called. (See Figs. 36 and 37.) The readjustment is possible at the higher temperature because of the greater atomic activity. Upon annealing, the hardness and strength of the strained metal are decreased, but its plasticity and workability are regained.

In annealing, the temperature should not be held too long at the point at which grain *growth* occurs, because abnormally large grains may be formed by some crystals extending their boundaries and absorbing neighboring crystals. The temperature at which this occurs varies with different metals, and other factors being equal, it will occur at lower temperatures if the metal is pure. An excessive enlargement of crystals may also be produced by holding the

metal for an extended period at the proper annealing temperature. The coarsening of structure that results from this cause is illustrated by Figs. 36 and 37.

Hot Working.—In effect, hot working is a combination of cold work and annealing. The grain size is decreased by hot working, but if the process is not continued until a temperature that is too low is reached, the crystals regain their symmetry, and the strained condition that would have been produced by the distortion is not apparent. The effect, then, is to harden and in some degree to strengthen the metal without seriously affecting the ductility.



Fig. 37.—Same alloy as shown in Fig. 12, after repeated annealing. 10 diameters. (*Law.*)

"Season" Cracking.—The brasses, bronzes, and some other alloys are subject to a type of failure known as "season" cracking. It is particularly likely to occur in brasses containing from 20 to 40 per cent of zinc, and it is practically always confined to alloys that have been forged or worked, especially cold-worked, in some form such as rivets, rods, tubes, and sheets. The cracks are found in articles that appear to be made of sound material and according to approved design. They develop some time after the piece has passed inspection, either in service under load or even before being put into actual service. They may vary in size from those of microscopic dimensions to those causing complete rupture.

The primary cause of season cracking is initial internal stresses introduced during manufacturing by processes designed to yield a "work hardness" to meet specifications for high tenacity, etc. Corrosion is a contributory cause due to the fact that localized stresses are brought into play at the bottom of the little corrosion pits and corrugations formed on the surface of the metal. Because the cracking develops so frequently in conjunction with corrosion, this type of failure is often spoken of as "corrosion" cracking. The cracking is augmented also by temperature changes.

In combating season cracking, the first step is to relieve the initial internal stresses by suitable heat-treatment. Stress-free material may be obtained by annealing for one hour at 400 to 550°C., but in some cases this leaves the metal too weak. The method of "springing," which consists of bending the bar backward and forward radially until all the outer fibers have been permanently lengthened, has been used with success. If the surface of the metal is kept highly polished, the failures are inhibited because localized stresses are eliminated to some extent.

Alloys of Copper

In this section the more important alloys containing a preponderance of copper will be discussed. They can be divided into two principal classes: the brasses and the bronzes. The brasses are primarily alloys of copper and zinc and the bronzes of copper and tin, but there are numerous modifications of them produced by the addition of smaller amounts of other elements. Many appear on the market under special trade names but no separate classification of these will be made here.

In addition there are the cupronickels, containing principally copper and nickel, and the nickel silvers (German silvers) in which the zinc of brass is partly replaced by nickel.

The Brasses.—Since these are primarily binary copper-zinc alloys, it is advantageous to consider first a somewhat simplified[1] equilibrium diagram for this system (Fig. 38). The solid liquid equilibria in this system are made up of a combination of five peritectic phase changes at successively lower temperatures with increasing percentages of zinc. This is possible because, in addition to the terminal α and η solid solutions, four intermediate solid solutions appear, designate as β, γ, δ, and ϵ. This gives rise to five two-phase solid equilibrium regions: $\alpha \rightleftharpoons \beta$, $\beta \rightleftharpoons \gamma$, $\gamma \rightleftharpoons \delta$,

[1] The $\beta \rightleftharpoons \beta'$ transformation in the solid state is omitted.

$\delta \rightleftharpoons \epsilon$, and $\epsilon \rightleftharpoons \eta$. Owing to the eutectoid reaction, $\delta \rightleftharpoons \gamma + \epsilon$, this reduces to four two-phase regions below 555°C., the δ phase disappearing at this temperature. Up to 39 per cent of zinc at room temperature the alloys will consist of a homogeneous α solid solution. From 39 to 46 per cent of zinc, the alloys will be two phase, a mixture of α and β solid solutions. From 46 to 50 per cent of zinc a single β phase appears, with higher zinc content γ appears and the alloys become too brittle to be of commercial use.

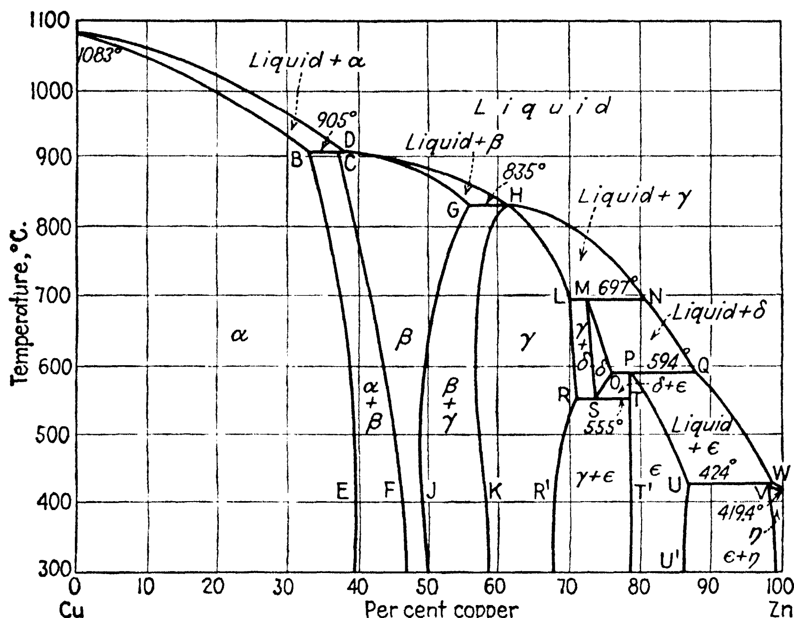


FIG. 38.—Equilibrium diagram for the copper-zinc system.

Classification and Properties of Brasses.—With a range of composition from 5 to 45 per cent of zinc, the brasses are among the most useful of alloys. They possess excellent mechanical properties, are corrosion resistant, and are readily machinable. A very satisfactory classification of these alloys is given in Table 43, abstracted from an article by D. K. Crampton in "The Metals Handbook," 1939 ed.

It will be observed that all the commercial brasses except Muntz metal consist of α solid solutions at room temperature. Examination of the equilibrium diagram will show, however, that in the cooling of a "high brass" (66 per cent of copper) some β may be retained metastably at room temperature in the cast metal, but

TABLE 43.—COMPOSITION, USES, AND PROPERTIES OF BRASSES

Name	Composition, %		Color	Typical uses	Temper	Tensile strength, psi	Elongation in 2 in., %
	Cu	Zn					
Muntz metal...	59	41	Reddish	Architectural work, welding rod, condenser tubes, valve stems	Hot rolled Cold rolled	54,000 80,000	45 5
Extruded rivet metal........	63	37	Typical brass color	Rivets, screws	Rivet	60,000	30
High brass.....	66	34		Stamping, blanking, drawing, spinning, forming, radiator cores, springs, screws, rivets, grill work, chains	Light anneal Soft anneal Hard Rivet Spring	53,000 46,000 76,000 60,000 125,000	54 64 7 30
Cartridge or spinning brass	70	30		Cartridges, eyelets, tubes, spinning, drawing	Light anneal Soft anneal Hard Spring	53,000 46,000 76,000 92,000	54 64 7 3
Brazing brass..	75	25		Drawing, spinning, springs; particularly suited for brazing	Light anneal Soft anneal Hard Spring	52,000 45,000 76,000 125,000	50 62 7
Low brass	80	20	Red gold	Drawing, forming, flexible hose	Light anneal Soft anneal Hard Spring	47,000 43,000 75,000 120,000	47 55 7
Rich low brass.	83	17		Fourdrinier wire	Soft	42,000	
Red brass......	85	15	Red	Hardware, radiator cores, plumbing pipe, condenser tubes, flexible hose	Light anneal Soft anneal Hard Spring	45,000 40,000 71,000 83,000	48 43 5 3
Commercial....	90	10	Bronze	Screen wire, hardware, trim, forgings, screws, rivets, costume jewelry	Light anneal Soft anneal Hard Spring	41,000 38,000 64,000 73,000	42 45 4 3
Gilding metal..	95	5	Copper	Drawing, spinning, forming	Light anneal Soft anneal Hard Spring	35,000 36,000 55,000 65,000	42 44 4 3

annealing below the two-phase region will redissolve it. All these α brasses show a high degree of plasticity in cold-working operations and are very useful materials of engineering construction. The Muntz metal brasses, consisting of α and β brass, are characterized by great plasticity at red heat, and they can be worked readily while hot by rolling, extrusion, and the like. At room temperature, on the other hand, they are not suitable for severe cold-working operations.

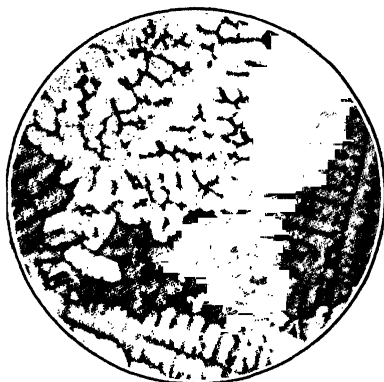


Fig. 39.—Brass containing 35 per cent of zinc as cast. 50 diameters. (*Bassett.*)

Alpha brass when cast exhibits the usual tendency of solid solutions to form dendrites or cored crystals (page 217). The appearance of grains of this kind is shown in Fig. 39. The struc-

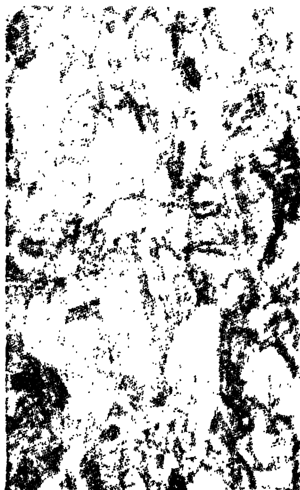


Fig. 40.



Fig. 41.

Fig. 40.—Deformed grains in brass reduced 50.9 per cent in thickness by cold rolling. Zinc content 32 per cent. 75 diameters. (*Bassett and Davis.*)

Fig. 41.—Equiaxed grains in brass of same composition as in Fig. 20. Reduction in thickness by cold rolling 50.9 per cent followed by heating at 650°C. 75 diameters. (*Bassett and Davis.*)

ture of the alloy when cold-rolled is shown in Fig. 40. Here the elongated form of the grains, typical of cold-worked brass, is clearly

marked. Figure 41 illustrates the equiaxed, polyhedral grains typical of cold-worked brass after annealing.

If a brass were wanted for tensile strength only, it should contain about 45 per cent of zinc. As shown by the curves in Fig. 42*a*, the tensile strength reaches a maximum with about this amount and

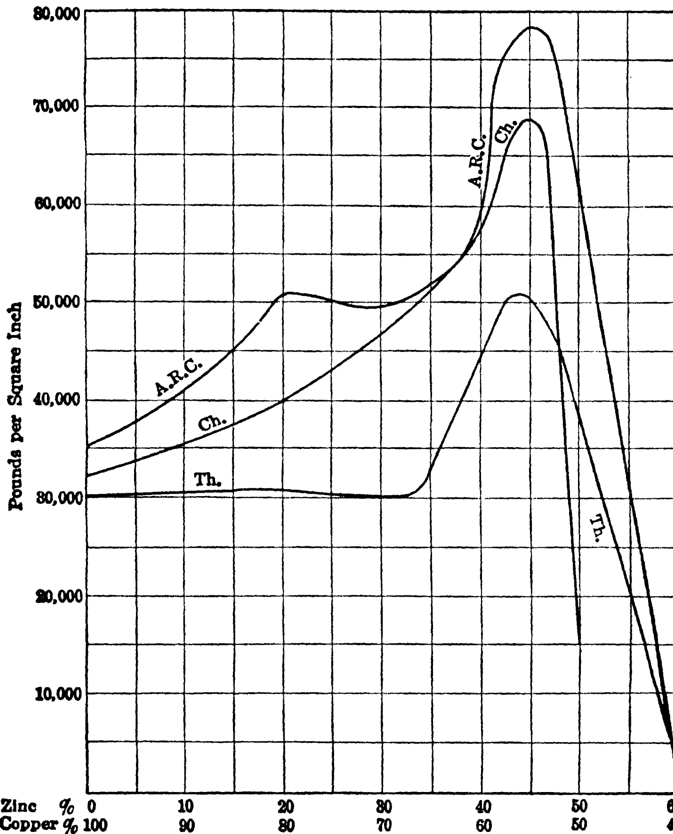


FIG. 42*a*.—Tensile strength of copper-zinc alloys. (*After Sexton.*) A.R.C.—Alloys Research Committee (worked rods). Th.—Thurston (castings). Ch.—Charpy (annealed brass).

then falls off sharply. It should be noted, too, that the strength varies greatly with the mechanical and heat-treatment that the alloy receives. Brass so proportioned, however, that the tensile strength is at the maximum, is very brittle as is shown by the low ductility with this composition in Fig. 42*b*. Ductility reaches a maximum with about 30 per cent of zinc, but when the beta con-

stituent appears, it rapidly decreases. Since a brittle alloy has very little value as a constructional material, some of the tensile strength must be sacrified in order to gain ductility and toughness. Consequently, the most generally serviceable brasses are those that contain not above about 40 per cent of zinc, as shown in Table 43.

Modified Brasses.—The mechanical properties or corrosion resistance of the brasses is in some cases greatly improved by the introduction of relatively small quantities of one or more other metals. Some of the more common of these additions will be noted.

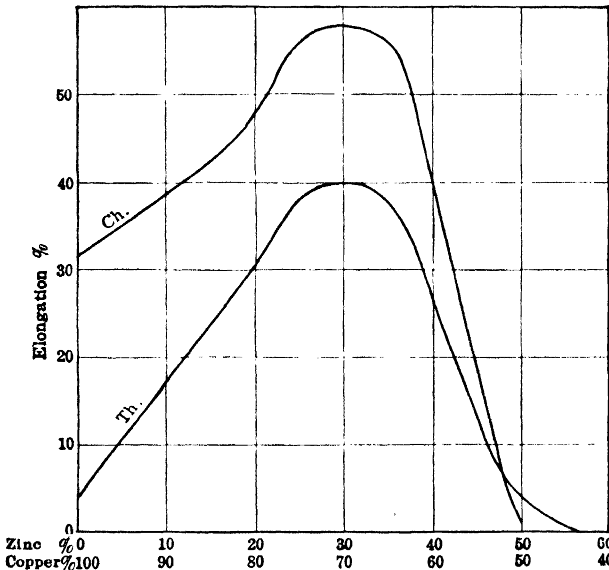


FIG. 42b.—Ductility of copper-zinc alloys. (*After Sexton.*) Th.—Thurston. Ch.—Charpy.

Aluminum Brass.—The amount of aluminum added to brass does not usually exceed 3 per cent. It raises the tensile strength but decreases the ductility. The product has a deep golden color and resists corrosion better than ordinary brass. It casts well and may be forged or rolled.

Tin Brass.—Tin is one of the most usual metals added to brass. It increases the hardness and tensile strength but the amount employed should not exceed about 2 per cent, because with higher amounts the ductility begins to decrease. Tin renders brass less liable to corrosion in sea water and, since on this account it is used in naval construction, the alloy is sometimes called *naval brass.*

An alloy of similar composition, consisting of approximately 38 per cent of zinc, 2 per cent of tin, a little iron, and the remainder copper, is known as *Tobin bronze.* This also is a very useful alloy of high tenacity, good working qualities, and excellent corrosion resistance.

Manganese Brass.—The alloy referred to under this head is generally spoken of as *manganese bronze,* but it is in reality a brass since the main constituents are copper and zinc. The composition varies considerably, but the following percentages may be regarded as typical: copper, 60 to 62 per cent; zinc, 38 to 42 per cent; tin, 0.5 to 1.5 per cent; iron, 0.5 to 1.5 per cent; manganese, 0 to 0.5 per cent; and sometimes a little aluminum. The manganese is generally added in the form of ferromanganese; this accounts for the presence of iron, which in itself has important effects. Manganese is very active in reducing the oxides of other metals, an action that is highly beneficial. In some instances, no manganese is shown on analysis because it has all been eliminated by the reactions of deoxidation. In addition to its action as a deoxidizer, manganese hardens and strengthens the alloy.

In cast form, the tensile strength of the manganese brass lies in the neighborhood of 70,000 psi and this is somewhat improved by working, as by rolling and forging. It is exceedingly tough and has a high resistance to corrosion even in sea water. It is used for pump rods, valves and cylinders, hydraulic rams, tubes, propellers, nuts, bolts, etc.

Iron Brass.—When iron is added to ordinary brass, it produces a hard, strong, and tough alloy which is easily cast. One of the most widely used alloys of this type is known as *delta metal,* which was brought out as a proprietary alloy. Under the original specifications, an iron-zinc alloy was first made containing about 8 to 10 per cent of iron, which in turn was combined in the proper ratio with copper; the combined metals were then deoxidized with phosphorus. The alloy as usually prepared contains 55 to 60 per cent of copper, 40 to 43 per cent of zinc, 1 to 3 per cent of iron, and fractional percentages of manganese and tin. Its tensile strength is about two-fifths greater than brass of similar composition with the iron omitted.

Lead Brass.—In brass that is intended for filing or turning, 1 to 2 per cent of lead is employed to prevent fouling of the tools and to cause the turnings to break more readily; this prevents clogging of automatic machines. Lead increases the softness of brass. It is sometimes added to brass that is to be worked, but care should be

taken to add but a small amount, because it reduces the ductility and strength. Only about 3 per cent will alloy with the brass; if more than this is added, it has a strong tendency to liquate. On this account "leaded" brasses should be chilled quickly when cast. Usually, lead in small amount is introduced accidentally from the spelter.

Arsenic, antimony, and bismuth may occur in brass, but when found, their presence is accidental. They are all objectionable because they are very active in producing brittleness.

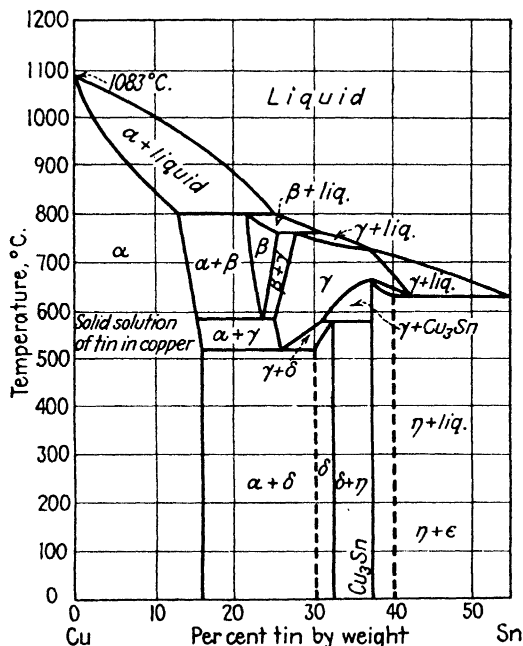


FIG. 43.—Equilibrium diagram for the copper-tin system.

Preparation of Brass.—According to the general principles for making alloys, the copper, having the higher melting point and being in excess, is melted first, preferably under granular charcoal. Then the zinc, previously warmed, is added to the melt in pieces small enough so that they do not chill the copper and cause it to solidify. If this should happen, zinc will be lost while awaiting the remelting of the copper. On the other hand, the temperature of the melted copper should not be too great, or the volatilization of zinc will be excessive. In some cases the crucible containing the

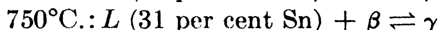
melted copper is removed from the furnace and the zinc in the melted state is slowly poured in with stirring. When all of the zinc has been added, the melt should be stirred thoroughly.

Since the melting point of copper is above the boiling point of zinc, a considerable amount of the latter will be lost through vaporization and oxidation in any case; the amount varies from about 5 to 10 per cent of that added, depending upon the care exercised. This loss must be taken into account in making brass to conform with given specifications. In remelting brass, zinc is also lost. As a result, remelted brass is always richer in copper than before remelting.

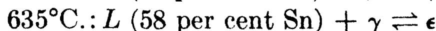
The Bronzes.—Bronze is essentially an alloy of copper and tin. The phase diagram for this system is quite complex and there is still disagreement over some of the regions. A somewhat simplified diagram is given in Fig. 43 covering the range up to about 50 per cent of tin. In this range, there are four solid solutions, α, β, γ, and ϵ involved in solid-liquid equilibria and the following peritectic phase changes appear:



$$798°\text{C.}: L \text{ (25 per cent Sn)} + \alpha \rightleftharpoons \beta$$

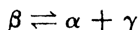


$$750°\text{C.}: L \text{ (31 per cent Sn)} + \beta \rightleftharpoons \gamma$$



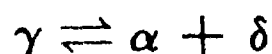
$$635°\text{C.}: L \text{ (58 per cent Sn)} + \gamma \rightleftharpoons \epsilon$$

The β phase disappears at 580°C. in the eutectoid reaction



$$\beta \rightleftharpoons \alpha + \gamma$$

and the γ in turn undergoes a eutectoid reaction at 520°C.:



$$\gamma \rightleftharpoons \alpha + \delta$$

Another unusual behavior is the appearance of the compound Cu_3Sn which separates from the γ solid solution as shown in the diagram. Although these phases are of interest from the theoretical side, only the α solid solution range is of practical importance, since the useful bronzes do not usually exceed 16 per cent of tin, which is the limit of the α region at room temperature. However, it is only in the well-annealed alloy that a homogeneous α solid solution will be found at this percentage of tin. Even a 9 per cent alloy, as cast, will not consist entirely of the α phase. During solidification, bronze, like brass, produces dendrites (Fig. 44) that are richer in copper than the equilibrium liquid. Thus the tin percentage is increased in the melt between the α dendrites until, with rapid cooling, this liquid may reach the peritectic composition and sepa-

rate β solid solution. This β phase, as shown above, undergoes a eutectoid reaction at about 580°C., forming α and γ, and this γ in turn gives α and δ in the eutectoid change at 520°C. Thus at room temperature this cast alloy contains α solid solution and δ solid solution, a hard brittle constituent, which increases the strength of the alloy but decreases its malleability and ductility. If the alloy is reheated to 700°C. for some time, diffusion takes place until homogeneous α bronze is formed. When cooled to room temperature after heat treating, it is found that the alloy is stronger and that its toughness is greatly increased.

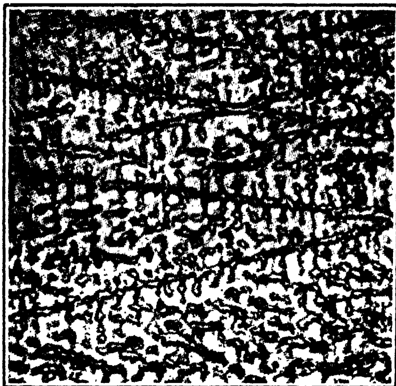


FIG. 44.—Gear bronze, rapidly cooled, showing dendrites of alpha solid solution of tin in copper. 50 diameters. (*Jeffries and Archer.*)

Effect of Composition on Physical Properties.—The tensile strength of bronze increases gradually with the amount of tin, reaching a maximum with about 20 per cent of tin, but as the tin increases beyond this amount the tensile strength very rapidly diminishes. Bronze is most ductile when it contains about 5 per cent of tin. With this amount it may be rolled satisfactorily at a red heat. Bronze is used chiefly for casting, however. As the amount of tin is increased above 5 per cent, the ductility gradually lessens and practically disappears with about 20 per cent of tin; since ductility is coordinate with toughness, these alloys are very brittle. They are also very hard. The most useful of the bronzes are those that contain from 8 to 11 per cent of tin, since the maximum *combined* strength and toughness are secured with about these amounts. Bronze containing tin within these limits was formerly known as *gun metal*, since because of its strength it was used for making guns, but now steel has entirely replaced it for this purpose. At the present time, the term gun metal is very loosely used and cannot be said to have any definite significance. As cast, the alloy containing 9 per cent of tin has a tensile strength of about 30,000 psi. The bronzes containing from 4 to 8 per cent of tin are used for coinage and medals. The copper-tin series of alloys containing between 15 and 25 per cent of tin is known as *bell metal*. Such

alloys are very hard and brittle, but are sonorous and are employed, therefore, in making bells and gongs. By alloying 2 parts of copper with 1 of tin, a very hard, brittle, white alloy is produced called *speculum metal.* When highly polished, it serves excellently for mirrors and reflectors.

Modified Bronzes.—The zinc bronzes usually contain 88 per cent of copper, 8 to 10 per cent of tin, and 4 to 2 per cent of zinc. The presence of the zinc in the bronze increases the fluidity of the melted metal and in this way tends to prevent gas flaws in the casting. It also increases the strength and ductility. As reported by Karr and Rawdon, the tensile strength of the 88-10-2 alloy when cast in sand was found to be about 38,000 psi; when annealed by heating to 700°C. for 30 min. and cooling in the furnace for 24 hr., the strength was not lessened and the ductility was greatly increased. The specific gravity when cast in sand is about 8.58; the melting point is about 980°C.

Phosphor Bronze.—It is a well-known fact that the desirable properties of metals and alloys are greatly benefited by thorough deoxidation. In the report of zinc bronze just mentioned, Karr and Rawdon point out that a microscopic examination of the fractured test specimens showed that the most common source of weakness was entrained or occluded oxides in the metal. Such oxides frequently occur as thin films in otherwise sound castings. The films produce brittleness and low ductility. By the reduction of these oxides with a suitable agent, the desirable properties of the alloy are much increased Because of the great readiness with which it combines with oxygen, phosphorus has been found to produce excellent results when used for this purpose.

Since phosphorus may be added to a bronze of any composition, the significance of the term *phosphor bronze* is quite indefinite. It is certain, however, that whatever good qualities the bronze might have, they are greatly increased by the addition of phosphorus. The tensile strength, the elasticity, and the resistance to fatigue are enormously increased; so much so that it may almost be considered as an entirely new alloy.

Phosphorus is best added to the bronze in the form of phosphor copper, a hard, brittle substance of white fracture, containing about 16 per cent of phosphorus; or as phosphor tin, a white, brittle, crystalline material containing about 6 per cent of phosphorus. Upon being added to molten bronze nearly all of the phosphorus oxidizes and escapes, so that most phosphor bronzes contain no

more than a few tenths of 1 per cent. The crystalline structure of two bronzes, one with and the other without phosphorus, as shown by the microscope, seems to be the same in both cases. Phosphor bronze is then essentially a deoxidized bronze.

Although phosphorus produces very beneficial results through its activity as a deoxidizing agent, if there is much of it left in the alloy, it may be a decided detriment. This residual phosphorus increases the hardness and brittleness of the bronze; the amount left, therefore, must be kept within low limits. When special hardness is desired there may be 1 per cent, but as much as 4 per cent makes the alloy useless.

Phosphor bronze of proper composition can be forged, drawn cold, rolled, and cast. It seems to resist corrosion better than ordinary bronze, especially by sea water, so that it is much used for propeller blades. On account of its toughness, elasticity, and strength, it may serve as a substitute for steel, as in the manufacture of corrosion-resistant mine cables, ship sheathing, valve parts, springs, etc.

Bearing Bronzes.—These are phosphor bronzes to which lead has been added. For ordinary bearings the amount of lead does not exceed 2 per cent. The lead is distributed through the alloy in small drops, acts as a lubricant, and at the same time improves the machinability. Where heavy loads are to be carried, *high-lead plastic bronzes* are used. These contain 70 to 85 per cent of copper, 5 to 10 per cent of tin, and 10 to 20 per cent of lead. If these alloys are rapidly cooled, the lead is uniformly distributed as spherical segregations.

Aluminum Bronze.—This contains 88 per cent of copper, 8 per cent of aluminum, 3 per cent of iron. 0.5 per cent of tin. Thus it is primarily a copper-aluminum alloy. The equilibrium diagram for this binary system is similar to the copper-tin diagram on the high-copper end, forming α solid solutions up to about 10 per cent of aluminum. These alloys have high strength, around 65,000 psi, and hardness, and in addition have marked resistance to corrosion. They are somewhat difficult to cast due to oxidation.

Silicon Bronzes.—These are a recent development. They are copper alloys containing up to 4 per cent of silicon and up to 1 per cent of manganese, with small amounts of tin, zinc, iron, and aluminum. They are obviously not true bronzes, since the tin content is very small. They are on the market under various trade names. These alloys are remarkable in that they have

the strength of soft steel and at the same time are corrosion resistant. They are employed in screws, bolts, pumps, tubing, and the like when corrosion conditions are severe.

Beryllium Copper.—This is another recently developed alloy, sometimes called beryllium bronze. It is copper containing 2 to 3 per cent of beryllium. It shows an annealed tensile strength when cold rolled of 100,000 psi. These alloys also can be heat-treated. By mechanical working at 800°C. a tensile strength of nearly 200,000 psi can be reached, with a Brinell hardness of 340.

Copper-nickel Alloys.—As previously discussed (page 214), copper and nickel form a continuous series of solid solutions over the entire range of composition. The high-copper alloys of technical importance are listed in Table 44, along with their uses.

TABLE 44.—USES FOR COPPER-NICKEL ALLOYS

Uses	Percentage of Nickel
Driving bands on projectiles	5
Bullet jackets	15
Coinage	25
Condenser tubing for corrosive conditions	30
Resistance wire—"constantan"	40

Several ternary and quaternary alloys containing copper and nickel are of importance. *Manganin*, a resistance wire with a very low temperature coefficient of resistance, consists of 80 per cent of copper, 5 per cent of nickel, and 15 per cent of manganese. *Nickel silvers* or *German silvers* are ternary alloys of copper containing from 5 to 45 per cent of zinc and from 5 to 30 per cent of nickel. They have fair strength, good plasticity, and low thermal conductivity. They are used extensively as the base metal on which silver is plated for tableware and for high-grade plumbing and hardware.

ALUMINUM ALLOYS

In recent years there has been a tremendous development of so-called *light alloys;* these are principally alloys of aluminum. Light alloys high in magnesium are becoming increasingly important. In the engineering field, great quantities of aluminum alloys are now employed. Some of the stronger ones, in the worked and heat-treated condition, may reach a tensile strength of as much as 63,000 psi or more. This is comparable with the strength of mild steel (page 355). When it is remembered that the tensile

strength of cast commercial aluminum is approximately 12,000 to 14,000 psi, the preparation of such alloys is in itself a noteworthy accomplishment, but when their lightness is taken into account, the achievement becomes even more important. The specific gravities of the aluminum alloys range from 2.55 to 2.85, which is approximately a third that of steel.[1] The growing importance of aeronautics has given increased impetus to the development of light and strong aluminum alloys, but they are employed extensively in many other industries as well, *e.g.*, in the manufacture of automobiles and railroad cars. Briefly summarized, the properties that recommend these alloys for a wide variety of uses are their low specific gravities, high thermal and electrical conductivities, pleasing appearance, and acceptable corrosion resistance. With regard to corrosion resistance, it should be noted that in the preparation of aluminum alloys, the elements commonly added to commercial aluminum usually lower its corrosion resistance. Manganese is an exception. An alloy containing 1.25 per cent of manganese has about the same corrosion resistance as commercial aluminum.

The aluminum alloys of technical importance can be divided into two classes: the *casting alloys* and the *wrought alloys*. When metals are cast in either sand or permanent molds (page 388), the solidification should occur over a sufficient temperature range to permit additional metal to enter the mold after the surface has solidified, thus preventing the formation of cavities and unsound castings. Except for the casting of large ingots or blocks, this is impossible with a pure metal that solidifies at constant temperature. For this reason, along with contributing special desirable properties, aluminum must be alloyed with other elements for satisfactory casting.

Casting Alloys.[2]—There are two important binary casting alloys: one contains copper and the other silicon as the alloying element. The equilibrium diagram for the high-aluminum side of the aluminum-copper system is shown in Fig. 45. An ω solid solution of copper in aluminum first forms, and at higher copper concentrations a eutectic between this solid solution and an intermediate θ solid

[1] Owing to the fact that the yield point (incipient deformation) is lower in the strong aluminum alloys than in steel, slightly larger sections of the aluminum alloys are employed in construction. The saving in weight, then, as compared to steel, is about three-fifths.

[2] "Metals Handbook," 1939 ed.

solution occurs at 548°C. The eutectic liquid contains 33 per cent of copper and the ω solid solution formed in the eutectic solidification contains 5.7 per cent of copper. An 8 per cent copper alloy, which is one commonly used, would solidify over a temperature range of about 100°C., as can be seen from the diagram. The solid alloy would contain primary ω, separated above 548°C. and the eutectic of ω and θ solid solutions. According to H. J. Rowe[1] about 50 per cent of the aluminum foundry output of castings is of this alloy. Small amounts of iron, silicon, and zinc are sometimes added. These alloys have fairly satisfactory mechanical

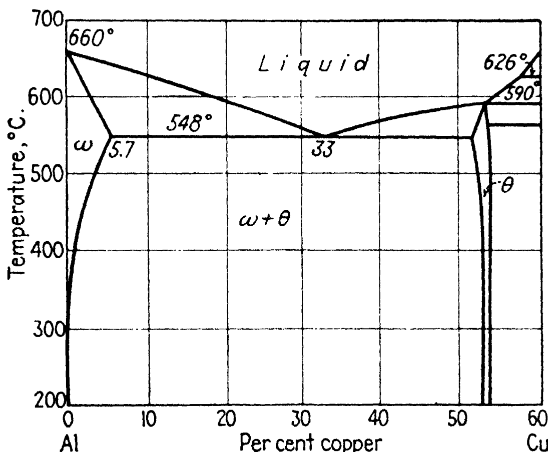


FIG. 45.—Equilibrium diagram for the aluminum-copper system.

properties, with a tensile strength around 20,000 psi and elongation of about 2 per cent in 2 in. They are readily machinable but do not have exceptional corrosion-resistant properties. These alloys are used extensively in the automobile industry for crankcases, transmission housings, and various fittings, and for household appliances such as vacuum cleaners, washing machines, and the like.

Four per cent copper casting alloys are also often used. From the phase diagram this alloy should solidify as a single-phase ω solid solution. At lower temperatures, however, due to a rapid decrease in solid solubility, θ solid solution should begin to precipitate. This precipitation would result in a hardening of the alloy; and from the temperature range at which these changes occur

[1] "Metals Handbook," 1939 ed., p. 1250.

these alloys lend themselves to heat-treatments that control the amount of precipitation and hence hardness. The tensile strength can be varied between 29,000 and 40,000 psi, and the hardness between 55 and 100 Brinell (10 mm. ball, 100 kg. load). These alloys frequently contain small amounts of iron and silicon.

The equilibrium diagram for the aluminum-silicon system is shown in Fig. 46. From this an alloy containing 12 per cent of silicon shows a primary separation of β solid solution which is pratically pure silicon, followed by solidification at 577°C., with

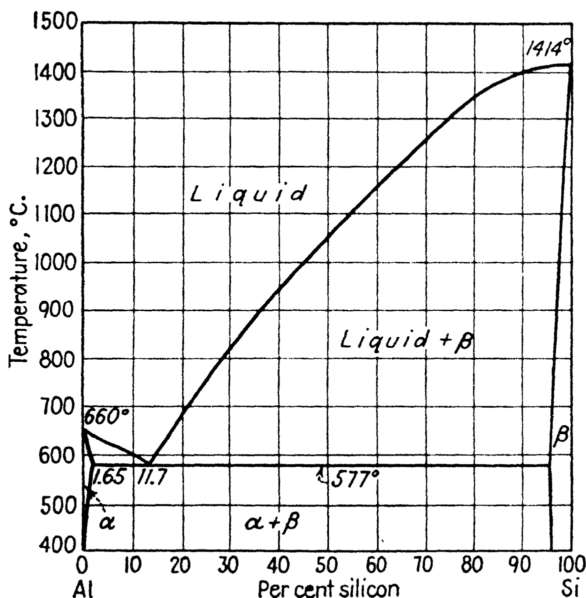
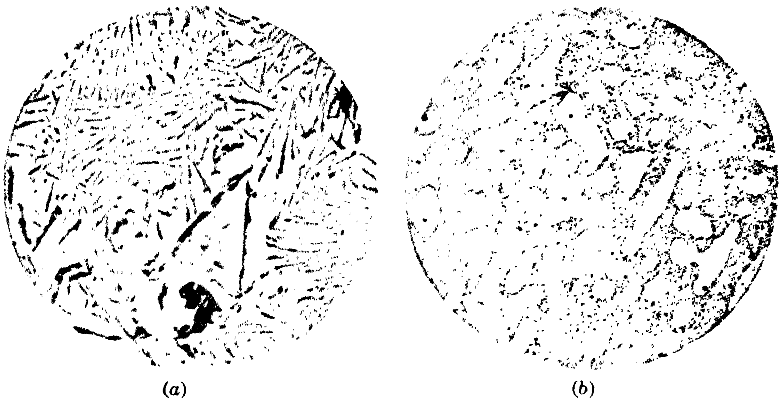


FIG. 46.—Equilibrium diagram for the aluminum-silicon system.

the formation of the eutectic mixture of α solid solution, containing 1.65 per cent of silicon, and β solid solution. A 5 per cent alloy solidifies with primary α followed by eutectic. Both these compositions are used technically. If a 12 per cent alloy is cast in the normal way, the silicon is found by microscopic examination to be present in rather large needles or plates. On the other hand, if the molten alloy is treated with an alkali fluoride or with a small amount of metallic sodium or potassium, the silicon particles (Fig. 47) are extremely fine. These are called *modified* silicon alloys and have a tensile strength around 26,000 psi. The silicon alloys have somewhat better casting characteristics than the copper alloys and in addition are much more corrosion resistant.

Magnesium also has been alloyed with aluminum to produce satisfactory casting alloys. With up to 15 per cent of magnesium, solidification occurs with the formation of a solid solution of magnesium in aluminum. The solid solubility, as with copper, decreases rapidly at lower temperatures with the separation of a second solid solution which is designated as α (Al-Mg). With 10 per cent of magnesium the alloy produced thus is heat treatable, since the amount of the precipitated α (Al-Mg) phase affects the mechanical properties. Along with having the lowest density of all aluminum alloys, a tensile strength of 43,000 psi can be achieved which is higher than that of any other aluminum casting alloy. These



(a) (b)

FIG. 47.—Castings of 12 per cent silicon in aluminum; (a) untreated, (b) modified. (*Homerberg and Williams.*)

alloys are used in railroad car construction, truck frames, and other applications where light weight, high strength, and good corrosion-resistant properties are desired.

A 4 per cent magnesium casting alloy is also employed technically. This has low density, fair mechanical strength (about 25,000 psi), good machinability and corrosion resistance.

There are several aluminum casting alloys containing three or even four alloying elements, which are used in special applications. Of the two that are used for automobile and airplane pistons one contains 10 per cent of copper, 1.25 per cent of iron, and 0.25 per cent of magnesium; the other 12 per cent of silicon, 1 per cent of copper, 1 per cent of magnesium, and 2.5 per cent of nickel.

Wrought Aluminum Alloys.—Wrought alloys are those which are brought to their final shape and form by such mechanical operations as hammering, cooling, drawing, or extruding (page 396).

These mechanical treatments tend to produce a fibrous structure (see Fig. 40, page 230) with high tensile strength and other improved properties. Ordinary commercial aluminum (page 134) of 99.0 to 99.3 per cent purity can be treated directly in this way. There are, however, two wrought aluminum alloys of particular importance today, of which *duralumin* is most extensively used. It has the following range of alloying constituents:

	Per Cent
Copper	3.5–4.5
Magnesium	0.3–1.0
Manganese	0.4–1.0
Silicon	0.3–1.0

This metal is suceptible of heat-treatment to produce a maximum tensile strength of 60,000 psi and is still highly ductile with an elongation of 19 per cent. This compares with the properties of a low-carbon steel (page 348), and yet this alloy has about one-third the density of steel. The heat-treatment of duralumin is described in more comprehensive metallurgical texts.

There are a number of other wrought alloys with desirable properties for certain applications. One, known as 24S, has mechanical properties somewhat superior to duralumin and contains 4.4 per cent of copper, 1.5 per cent of magnesium, and 0.6 per cent of manganese.

Age Hardening.—In the discussion of the aluminum alloys frequent reference has been made to heat-treatments that improve their mechanical properties. These treatments in general entail heating of the metal to some higher temperature, then quenching to a lower temperature, and holding for definite periods. At these lower temperatures a change in mechanical properties takes place with time. This process is known as *age hardening*. As indicated before, it occurs due to the precipitation of a second phase from a homogeneous solid solution as a result of decreased solid solubility at lower temperatures. It should be noted that for maximum hardness a certain critical size must be reached by the precipitated particles. It has been found that as aging proceeds the hardness increases with time up to a maximum value and then decreases. The hard precipitated particles act as "keys" and interfere with the movement of the crystal fragments along the slip planes. This is shown diagrammatically in Fig. 48*a*. The figure represents an idealized section through a crystal, and it will be noted that with the arrangement shown, every plane of potential slip encounters

at least one of the particles. The motion of all of the planes, therefore, is mechanically obstructed.

The size of the particles is important. If all the particles shown in Fig. 48*a* were gathered together in a single large particle as shown in Fig. 48*b*, although the strength of the single "key" would be increased, many planes would not be intercepted by it. They would, therefore, be free to move. On the other hand, if the particles were too small, they would become less effective. There is obviously, a certain size of the particles that hinders to the greatest degree the movement of the planes; this is known as the critical size, or the diameter at critical dispersion. It is estimated

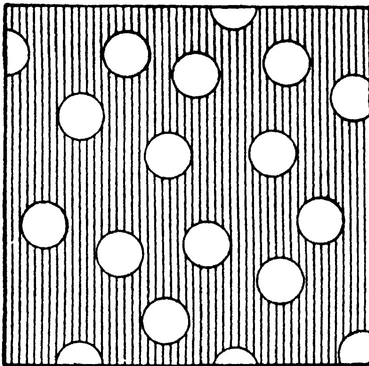


Fig. 48*a*.—Slip planes keyed by hard particles. (*Jeffries and Archer.*)

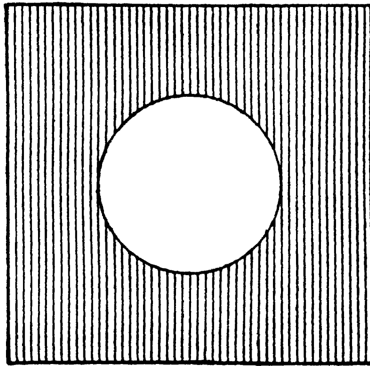


Fig. 48*b*.—Hard constituent gathered into a single particle leaving many planes unkeyed. (*Jeffries and Archer.*)

by Jeffries and Archer[1] that the average diameter of the particles at critical dispersion is of the order of 10^{-7} cm. The hardening of duralumin (page 244) by heat-treatment is accounted for by the precipitation of hard particles of the compound $CuAl_2$. Hardening produced in this manner is called *precipitation hardening.*

It should be mentioned that, in some cases, age hardening occurs without any physical evidence of actual precipitation. Various explanations have been offered for such behavior, based mainly on the assumption that considerable segregation of atoms may occur in the lattice of the parent solid before precipitation occurs. This gives rise to knotty distortion of the lattice and increase in the hardness.

[1] Jeffries and Archer, "The Science of Metals," p. 82, McGraw-Hill Book Company, Inc., New York, 1924.

Magnesium Alloys

Magnesium alloys or Dowmetals have become of great importance in recent years because of the demands for metals of light weight, good strength, and corrosion-resistant properties. The specific gravities of the higher magnesium alloys, used technically, range from 1.76 to 1.86 compared to 2.55 to 2.85 for the aluminum alloys. Because of this lower density the strength of some of the Dowmetals, weight for weight, is equal to or even superior to the aluminum alloys.

The magnesium alloys used in this country contain no more than 10 per cent of alloying elements the chief of which is aluminum, which ranges from 4 to 8 per cent. Some of the alloys contain zinc up to 3 per cent and all contain 0.2 to 0.3 per cent of manganese. Table 45, condensed from that of John A. Gann in "Modern Uses of Non-ferrous Metals,"[1] gives the compositions and properties of the more important alloys.

Table 45.—Composition and Properties of Magnesium Alloys

Alloy	Alloying elements, %			Treatment	Tensile strength, psi	Elongation in 2 in., %	Brinell hardness
	Al	Mn	Zn				
Dowmetal H	6.0	0.3	3.0	Cast	28,000	6	48
				Cast; heat treated*	35,000	10	51
				Cast; heat treated†	40,000	5	68
Dowmetal F	4.0	0.3	...	Extruded rod	40,000	16	48
Dowmetal J	6.5	0.3	0.8	Extruded rod	43,000	18	55
Dowmetal A	8.0	0.2	...	Extruded rod	47,000	13	58

* Solution heat-treatment.
† Solution heat-treatment plus precipitation heat-treatment.

Nickel Alloys

It has been pointed out that nickel and copper form a continuous series of solid solutions (page 214), and the alloys containing up to 40 per cent of nickel have been considered (page 239). On the high-nickel side the most important alloy is *Monel*

[1] Published by A.I.M.E., New York.

metal, the direct production of which from nickel-copper matte is considered on page 179. This alloy contains about 67 per cent of nickel and 28 per cent of copper with the balance mainly iron with small percentages of manganese, silicon, and carbon (up to 0.26 per cent).

By increasing the iron and manganese contents, modifications of Monel metal are produced with special properties. The addition of aluminum makes an alloy of especially satisfactory mechanical properties, known as "K" Monel metal.[1] Monel metal has great corrosion resistance and is used in diversified applications, including pickling equipment in the steel industry, dye vats, sinks, hot-water boilers, and kitchen and food-processing equipment. It is employed also in making valves, agitators, pump rods, and other apparatus used in chemical, petroleum, and paper industries where corrosion conditions are severe.

The use of nickel as an alloying element in steels and cast irons is discussed in Chap. VII. There are, however, several nickel-iron alloys containing chromium and other metals that have very special and desirable properties. Some of these are listed below.

1. Heat-resisting and Electrical Resistance Alloys.—To meet the industrial demand for alloys to withstand temperatures up to 1000°C. (1800°F.) without oxidation, and at the same time maintain satisfactory mechanical properties, a number of alloys of nickel with iron and chromium have been developed. These have various trade names and compositions ranging up to 65 per cent of nickel. A complete list of these alloys is given in the "Metals Handbook," 1939 ed., pages 38 to 53.

For electrical heating units, such as resistance furnaces, stoves, and domestic heating appliances, a series of electrical resistance alloys have been developed which can be operated up to 1000°C. without appreciable oxidation or rapid deterioration. *Nichrome* and *chromel*, well-known examples, contain about 62 per cent of nickel, 15 per cent of chromium, and the remainder iron with small amounts of carbon.

2. Low Thermal Expansion Alloys.—These are the "Invar"-type iron-nickel alloys containing 30 to 40 per cent of nickel. Their coefficients of linear expansion are about one-tenth that of steel. They are used in measuring tapes, instruments, watches, and for bimetallic thermostat elements. An important application is in

[1] STANLEY, "Nickel, Past and Present," International Nickel Co., Inc., New York.

struts for aluminum alloy pistons (page 243). The compositions of these alloys are given in Table 46.

3. Magnetic Alloys.—These contain iron, nickel, and sometimes cobalt and have exceptionally high magnetic permeability at low field strengths. The compositions of these alloys also are given in Table 46.

TABLE 46.—COMMERCIAL HIGH-NICKEL ALLOYS

Name	Composition,* %						Characteristic properties
	Ni	Co	Cr	W	Al	Cu	
Invar	36	....	..	..	..	..	Low expansion from 0 to 200°F. (−18 to 100°C.)
Superinvar	31	5	..	..	..	..	Zero expansion near room temperature
Elinvar	32	....	5	2	..	..	Low thermoelastic coefficient
Dumet	42	....	..	..	..	..	For sealing in soft glass
Kovar	29	17	..	..	..	..	For sealing in hard glass
Platinite	46	....	..	..	..	..	Expansion same as platinum
Permalloy	78.5	....	..	..	..	..	High permeability at low field strengths
Hipernik	50	....	..	..	..	..	High permeability at higher field strengths
Perminvar	45	25	..	..	..	..	Constant permeability over a range of flux densities
Alnico I	20	5	..	..	12	..	Permanent magnet of high magnetic hardness
Alnico II	17	12.5	..	..	10	6	Same as above
Alnico III	25	....	..	..	12	..	Same as above
Alnico IV	28	5	..	..	12	..	Same as above

* Balance of composition is mostly iron.

BEARING METALS

The friction between two metals is directly proportional to the pressure applied. Of course, this is true only when both surfaces are sufficiently hard so that one does not gouge or rub into the other. The amount of the load that can be borne before gouging begins is greater, the harder the metals. Arguing from this point, to reduce friction and avoid cutting, hard surfaces should be used for bearings. This is true, but only under perfect adjustment. In an ordinary bearing there are points of greater and lesser pressure, and therefore of friction; hence the bearing must be sufficiently soft to mold itself about the shaft. But it must be able to resist

wear as much as possible also. The best fulfillment of these requirements has been obtained by the use of an alloy containing hard grains in a soft matrix. The soft matrix allows an adjustment, so that local pressures, which are generally responsible for trouble, are avoided; the hard grains on the surface resist the wear. This structure is found in the so-called "white alloys," which consist of lead, tin, antimony, copper, etc.

White Alloys. 1. *The Lead-antimony Alloys.*—These two metals alloy readily in all proportions; the hardness and brittleness of the product increase with the amount of antimony. The equilibrium diagram for this system is given on page 219. There is a eutectic

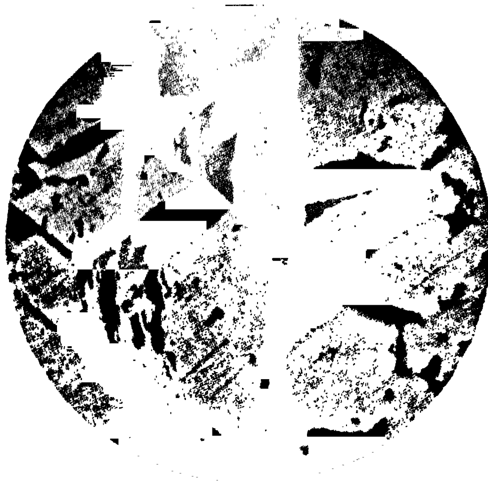


Fig. 49.—Lead-antimony alloy, containing 40 per cent of lead, etched with picric acid. Bright crystals of antimony surrounded by eutectic. 100 diameters. (*Gulliver.*)

at 13 per cent of antimony. With less antimony than this the structure of the alloy is made up of primary crystals of the soft α solid solution in the hard $\alpha + \beta$ eutectic. With antimony higher than 13 per cent the primary crystals are the hard β solid solution in the softer eutectic, as shown in Fig. 49. This latter structure fulfills the requirements of a good antifriction metal. As much as 15 to 20 per cent of antimony is advantageous in some cases, as for very heavy pressures.

2. The *tin-antimony-copper alloys* are called "Babbitt metal." They are more expensive than the preceding, because they contain a large amount of tin, but for the same reason they are considerably better. The tin becomes a constituent of the hard grains, diminish-

ing their hardness, it is true, but also their brittleness. The tin enters the matrix also and increases its compression strength. The structure of the Babbitt metal is made up of a mass of tin-containing cubical crystals of tin-antimony alloys, and needlelike crystals of an antimony-copper alloy, as shown in Fig. 50.

An alloy having the same composition as Babbitt's original alloy is made by first melting together the following: copper, 4 parts; tin, 12 parts; antimony, 8 parts; and then adding 12 parts of tin after fusion. The antimony and the first portion of the tin are



FIG. 50.—Tin-copper-antimony bearing metal. (*Law*.)

melted together, then the copper is added, and finally the remainder of the tin. This is called the hardening alloy. The bearing metal proper is made by melting 1 part of this alloy with twice its weight of tin, which makes a final alloy having the following composition: copper, 3.7 per cent; antimony, 7.4 per cent; and tin, 88.9 per cent.[1]

The Leaded Bronzes.—Bronzes to which a considerable amount of lead has been added are also used as bearing metals (page 238), but their structure is the reverse of the white alloys, since they consist of soft grains in a hard matrix. They are inferior to the white alloys as bearing metals, because they are less plastic and do not mold about the shaft so well. Although they are stronger than the white alloys, this fact does not allow them to bear heavier loads, because they have a greater tendency to "cut."

[1] For detailed directions for making Babbitt alloy, see *Foundry*, data sheet 81, January, 1911.

A leaded bronze that is used to a considerable extent for bearings has the following composition: copper, 64 per cent; tin, 5 per cent; lead, 30 per cent; and nickel, 1 per cent. This is known as plastic bronze; although it is not so plastic as the white alloys, it is more plastic than an ordinary bronze.

The structure of the plastic bronze is largely determined by the fact that lead does not alloy much with copper or with bronzes having a low tin content, and therefore remains to a large extent as an independent constituent in the bronze. The copper-tin alloy becomes the matrix in which the grains of lead are held. The small amount of nickel probably lessens the segregation of the lead by causing the alloy to solidify at a higher temperature. Aside from the fact that the presence of lead increases the plasticity of the bronze, the soft granules wear more rapidly than the harder matrix and form cavities in which the lubricant may be held.

Solders and Brazing Alloys

Solder is a readily fusible alloy used to join the surfaces of metals. Its joining ability depends upon the fact that a surface alloy is formed between the solder and the parts soldered. Soldering may be accomplished by means of various alloys, the composition of which depends upon the melting point desired and the metals to be joined. The most common solder, however, is an alloy of tin and lead, known as *soft* or *tinner's solder*. This is used for a great variety of purposes.

Physical Structure of Soft Solder.—The equilibrium diagram for the lead-tin alloys is shown in Fig. 51. As is indicated there, those alloys containing no more than 19.5 per cent of tin, or no more than about 2.6 per cent of lead, solidify as solid solutions. All the other alloys of these two metals solidify with the formation of the eutectic as is shown in the figure; the eutectic contains approximately 38 per cent of lead. As the tin content of the commercial lead-tin alloys ranges from about 25 to 75 per cent, the structure of these alloys consists of primary crystals of either α or β solid solutions, depending upon the proportions used, held in a matrix of smaller crystals of the eutectic.

Composition and Properties.—The tensile strength of solder is greatest with 72.5 per cent of lead, but this alloy is not sufficiently fusible to be used for general soldering. Any of the alloys that contain above 70 per cent of lead have a melting point too high to be used in ordinary soldering with a copper tool, although they may

be used with a steel one. The chief use to which such alloys are put is for coating iron or steel sheets for roofing, for filling hollow castings, etc.

The alloy that contains about 67 per cent of lead is used for plumber's solder; it will be discussed later under that head. The alloys containing from 55 to 60 per cent of lead melt from about 215 to 230°C., and are sufficiently fusible and freely flowing for ordinary soldering. That which contains 58 per cent of lead is used to a considerable extent for soldering joints in electric wiring because it is considered an easily flowing solder.

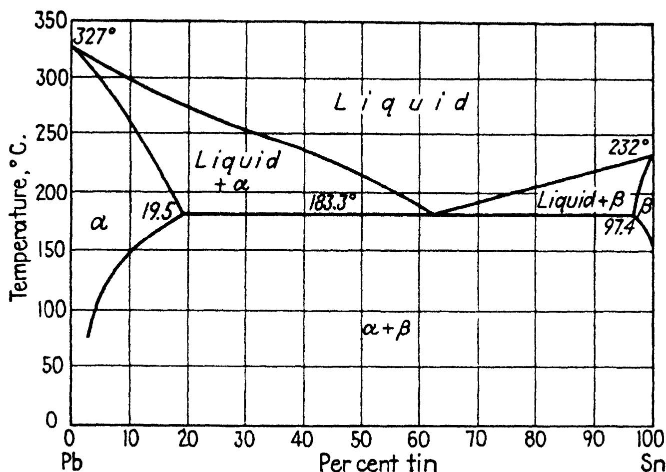


FIG. 51.—Equilibrium diagram for the lead-tin system.

But by far the favorite alloy with those who use solder is that which contains 50 per cent of lead and 50 per cent of tin; it is known commonly as "half and half." This alloy melts rapidly, flows freely, and presents a bright surface when the joint is finished. It can be used for every purpose to which soft solder is applicable, except "wiping joints," as it is technically called, in plumbing. But all kinds of work do not require a solder as high in tin as this, even though, because of its many good properties, it is much desired by the user. Its high price is a very great objection. Since the consumer desires to buy solder cheaply, it happens that many grades of solder appear on the market designated as "half and half" that contain much less than 50 per cent of tin. Very often the upper limit of the amount of tin contained in the "half and half" solder is determined by the price the customer is willing to pay.

TABLE 47.—SILVER SOLDERS

Composition, %				Melting point		Uses
Ag	Cu	Zn	Cd	°C.	°F.	
10	52	38	....	820	1510	Used for practically all nonferrous alloys (except aluminum) and steels and iron
20	45	35	....	775	1430	
80	16	4	....	740	1360	
45	30	25	....	675	1250	
50	15.5	16.5	18	630	1160	Special low melting
5	....	....	95	340	640	
5	....	16.6	78.4	250	480	

TABLE 48.—BRAZING ALLOYS

Composition, %	Mean melting point, °F.	Uses
Cu, 50; Zn, 50	1600	Strong connections on steel, cast iron, brass, bronze, nickel alloys
Cu, 45; Zn, 50; Sn, 5	1575	Stronger than above
Cu, 33; Zn, 60; Sn, 7	1400	Moderate strength
Cu, 93; P, 7	1300	

TABLE 49.—COPPER ALLOY WELDING RODS

Composition of elements other than Cu, %	Melting point, °F.	Uses
Zn, 40; Sn, 1.0	1625	For oxyacetylene welds. Strength, 50,000 psi
Zn, 40; Sn, 1.5; Mn, 0.75	1000	Harder and more wear resisting than above
Si, 4; P, 0.4	1860	Oxyacetylene welds on copper, brass, bronze, nickel alloys. Very strong
Sn, 10; P, 0.4	1900	Good strength and wear resistance. Applied by arc on copper, bronze, steel, nickel alloys
Ni, 30; Mn, 0.15	2235	Oxyacetylene, or carbon arc. Used on similar base metals

For some purposes, as for manufacturing gas meters, electrical instruments, etc., where a bright, freely flowing solder is desired, in order that all joints may be completely filled with the solder, greater amounts than 50 per cent of tin are used. As is shown in Fig. 51, the melting point of the alloy falls gradually with increase of tin up to the amount of 62 per cent. This is the eutectic alloy and melts at 183.3°C., the lowest temperature at which any alloy of lead and tin will melt completely.

Plumber's solder contains usually 67 per cent of lead and 33 per cent of tin. As this alloy cools through its solidification range, as shown in Fig. 51, it acquires a plastic condition, in which it has about the consistency of baker's dough, before it cools enough to grow hard. While in this plastic state, it may be molded into shape in the so-called "wiping of joints." Solders may be used in this way that contain from 60 to 67 per cent of lead. The 60 per cent alloy begins to assume the plastic state at about 235°C., and the 67 per cent alloy at about 243°C. The final solidification of both takes place at 183°C., the eutectic point, so that there is a range of about 55 to 60°C. during which they are plastic.

Brazing Alloys.—It is frequently necessary to join metals by the use of "solders" which, although they melt below the melting points of the metals being joined, still have melting points much above those of the lead-tin solders. At the same time joints of greater strength are produced. Various alloys of copper are used for this purpose and the process is known as *brazing*. There are three classes of brazing alloys in common use, with a melting range from 680 to 1240°C. (1250 to 2235°F.). These are presented with compositions, melting points, and uses,[1] in Tables 47, 48, and 49.

Aluminum Solder.—For aluminum, the solders most generally used are the tin-zinc alloys. The tin may range from 50 to 75 per cent, with the remainder zinc. An alloy consisting of 8 to 15 per cent of zinc, 5 to 12 per cent of aluminum, and the remainder tin has also been found satisfactory. A cadmium-zinc alloy, containing 40 per cent of cadmium and the remainder zinc, although more difficult to melt than the preceding alloys, has better corrosion resistance. With regard to corrosion resistance, pure zinc is the best aluminum solder, but it is somewhat difficult to work.[2]

[1] "Metals Handbook," 1939 ed., p. 1211.

[2] EDWARDS, FRARY, and JEFFRIES, "The Aluminum Industry," Vol. II, p. 463, McGraw-Hill Book Company, Inc., New York, (1930).

In using these solders, the edges to be joined are filed or are scraped clean. If the article will allow it, it is heated with a torch or similar device to a temperature at which the solder will melt; then the edges are rubbed briskly with a stick of the solder. If the object cannot be heated in this manner, the edges are heated with a tinned copper tool and the solder is rubbed on as before described. No flux of any kind is used. When the melted solder has run well over the surfaces to be joined, they are held pressed firmly together until the solder has solidified.

In no case should much dependence be placed on a soldered aluminum joint. This is particularly true if the work is exposed to the weather or to a damp atmosphere. Aluminum solders are cathodic (page 414) to aluminum, and, in the presence of moisture, an electrolytic action is developed that causes the joints to disintegrate. There is no solder for aluminum of which this is not true.[1]

Fluxes for Soldering and Brazing.—The value of a flux depends upon its ability to gather up, by dissolving or otherwise, the oxide or other adherent matter on the surface of the metal. It must stay in place also and keep away the oxygen of the air so that further oxidation cannot take place before the solder can be made to flow over the cleaned surface and alloy with it. If the metal were cleaned mechanically, as with a file, a film of oxide, imperceptible to the eye, would spread over the surface of the metal before the solder could be applied. Solder cannot alloy or combine with metallic oxides. In the method described for soldering aluminum, although the metal becomes oxidized after it is cleaned by filing or scraping, this relatively thin oxide layer is removed at the moment the melted solder is applied by rubbing with the stick of solder itself.

For use with the ordinary lead-tin solder, *zinc chloride* is a very serviceable flux for practically all the common metals and alloys. It does not serve for aluminum, however, because the oxide on aluminum forms so readily and adheres so tenaciously that some special method, such as that previously described, must be used. Zinc chloride may be employed in the form of a solution, as a paste made of the salt slightly moistened with water, or as a paste made by stirring the finely divided salt into Vaseline. Instead of using Vaseline, a mixture of fats such as *olive oil* and *tallow*, either with or without *rosin*, may be employed. The fats and the rosin are

[1] "Solders for Aluminum," *Nat. Bur. Standards, Circ.* 78, March, 1923.

first melted together and the zinc chloride is then stirred in. Sometimes ammonium chloride is used to replace part of the zinc chloride. Rosin alone, though not so satisfactory, is used as a flux particularly for outside work where the corrosive action of residual chlorides might be objectionable.

For brazing and silver soldering a mixture of borax and boric acid is used as a flux. This forms fusible borates with metallic oxides and at the same time supplies an adherent nonvolatile layer to prevent further oxidation. When metals that are high in silicon or nickel are being brazed, a bifluoride is added to the borax.

Die-casting Alloys

In die casting (page 393), a permanent water-cooled steel mold or "die" is used. This is mounted above a crucible carrying the molten alloy and a mechanical device injects or squirts just sufficient metal into the mold under pressures of from 400 to 5,000 psi. The die is filled in a fraction of a second and very rapid solidification occurs. Extreme dimensional accuracy is thus secured and small thin-walled castings can be produced rapidly. Die casting is used in the manufacture of parts for various types of household and automotive appliances. Some of the aluminum casting alloys previously described are suitable for die casting, as are some of the Dowmetals.

Tin-base Die-casting Alloys.—A number of such alloys are in use today. A partial list[1] with their compositions is given in Table 50. It will be noticed that these alloys are of the Babbitt-

Table 50.—Tin Alloys Used in Die Casting

Composition, %				Melting range, °F.	
Sn	Pb	Sb	Cu	Solid	Liquid
92	..	5.5	2.5	430	590
91	..	4.5	4.5	433	680
86	..	7.5	6.5	460	670
79	5	9	7	440	610
60	35	5	...	355	380

metal type and, although there are other applications, many bearings are still made by die casting. The tensile strength of these

[1] Gonser, "Metals Handbook," 1939 ed., p. 1734.

alloys ranges from 10,000 to 18,000 psi, and the die-casting method produces a desirable fine-grained structure.

Zinc Die-casting Alloys.[1]—These metals are extensively used today. There are three standard compositions specified by the A.S.T.M. They consist of zinc alloyed with from 3.5 to 4.5 per cent of aluminum and from 0.1 to 2.5 per cent of copper. These alloys, using low-cost materials, have low melting points, around 380°C. (715°F.), and at the same time have excellent mechanical properties. The tensile strength is about 45,000 psi, with elongation of 5 per cent in 2 in. They can be die-cast to an accuracy of ±0.002 in. per in. of length and castings weighing as much as 30 lb. have been produced.

They are used for automobile body hardware, carburetors, fuel pumps, speedometer frames, gears, refrigerator parts, small motor frames, radio chassis, and various housing equipment.

Low-melting Alloys[2]

This term is applied to alloys melting below 200°C. (390°F.). They are usually ternary or quaternary alloys of the low-melting metals, bismuth, cadmium, lead, tin, and sometimes mercury. By proper adjustment of composition, melting points ranging from 60 to 183°C. (140 to 361°F.) can be obtained. A complete list is given in the accompanying reference. The best known are Wood's metal (Bi, 50; Cd, 12.5; Pb, 25; Sn, 12.5), which melts at 68°C., and Rose's alloy (Bi, 50; Pb, 28; Sn, 22), which melts at 100°C. These alloys are used as low-melting solders, and in automatic sprinkler systems for fire protection. They are even used for certain types of castings and for dental work.

An interesting recent development is Matrix Alloy,[3] melting at 105°C. (221°F.), which contains 48 per cent of bismuth, 28.5 per cent of lead, 14.5 per cent of tin, and 9 per cent of antimony. This alloy is used to mount different parts of complex punches and dies by pouring the molten metal around these parts. It does not shrink on solidification, has a Brinell hardness of 19, and a tensile strength of 13,000 psi. This alloy will withstand continuous loads of 5 tons per sq. in.

[1] ANDERSON and STERN, "Metals Handbook," 1939 ed., p. 1770.

[2] VAN HORN, "Metals Handbook," 1939 ed., p. 1328.

[3] SMITH, "Modern Uses of Non-ferrous Metals," A.I.M.E., New York, 1935.

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CHAPTER VI

PRODUCTION OF IRON AND STEEL

By J. C. Warner, Ph.D.

The manufacture of iron and steel is one of the major process industries of the world because of the first-rate importance of these products as materials of construction. In 1929 about 96 million long tons (2,240 lb.) of pig iron were produced in the world, of which 42 million tons were produced in the United States. World production declined to a low of about 40 million tons in 1932 and since that time has steadily risen. In 1929, steel production in the world amounted to about 85 million long tons, over half of which was produced in the United States. Since 1900, iron and steel have been the most important of our engineering materials and, inasmuch as the properties of these materials frequently depend upon the method of manufacture, it will be profitable to devote some space to the processes for making them.

BLAST-FURNACE PRODUCTION OF PIG IRON

The iron blast furnace is a very efficient device for reducing iron ore to pig iron by a continuous process. The blast furnace normally requires as raw materials: iron ore, coke, limestone, preheated compressed air, and cooling water. It produces various grades of pig iron, slag, and blast-furnace gas.

Raw Materials for the Blast Furnace

Iron Ores.—Any iron-bearing mineral from which iron may be extracted profitably is an iron ore. The principal iron-bearing minerals in ore beds used at present, together with the chemical formulas and the iron contents of the pure minerals are given in Table 51.

Iron ores as mined, or even ores that have been subjected to beneficiation[1] by drying, washing, jigging, magnetic separation, etc., are composed not only of the pure minerals listed in Table 51 but

[1] Boylston, "Iron and Steel," 2d ed., pp. 49–51, John Wiley & Sons, Inc., New York (1926).

TABLE 51.—MINERALS IN IRON ORES

Name		Formula	Iron, %
Mineralogical	Chemical		
Magnetite	Ferrosoferric oxide	Fe_3O_4	72.4
Hematite (red)	Anhydrous ferric oxide	Fe_2O_3	70.0
Limonites (brown hematites):	Hydrous ferric oxides	$Fe_2O_3 \cdot xH_2O$	
Turgite	...	$2Fe_2O_3 \cdot H_2O$	66.0
Goethite	...	$Fe_2O_3 \cdot H_2O$	63.0
Limonite	...	$2Fe_2O_3 \cdot 3H_2O$	60.0
Xanthesiderite	...	$Fe_2O_3 \cdot 2H_2O$	57.0
Limnite	...	$Fe_2O_3 \cdot 3H_2O$	52.0
Siderite	Ferrous carbonate	$FeCO_3$	43.8

invariably contain in addition noniron-bearing substances known as the "gangue" of the ore. This part of the ore varies in amount and composition in the various deposits, and its character[1] is important in determining the value of an ore.

In addition to the factors already suggested, the value of an ore will be determined by the cost of mining, its location with respect to the other essential raw materials, such as coking grades of coal and limestone, the location of markets for iron and steel products, and transportation facilities for raw materials and finished products. Thus an ore deposit that is very desirable from the standpoint of its physical and chemical characteristics may be so located that it cannot be worked with profit. On the other hand, an ore that is inferior may, due to its favorable location, be smelted in competition with higher grade ores. For example, the lower grade Alabama ores can compete with the Lake Superior ores because ore, coal, and limestone are located close together in the vicinity of Birmingham.

Of the iron ore mined (1918–1928) in the United States[2] 84.5 per cent was produced by the Lake Superior region and 9.4 per cent by the Birmingham district. It has been estimated that the world supply of available ore of a quality similar to that now being used is roughly 58 billion tons—enough to last about 900 years. About one-sixth of this supply lies within the United States. In addition there are enormous reserves of lower grade ores. For example,

[1] CAMP and FRANCIS, "The Making, Shaping and Treating of Steel," 5th ed., Carnegie-Illinois Steel Corp., Pittsburgh, Pa., pp. 72–74 (1940). This excellent book hereafter will be referred to as Camp and Francis, 5th ed.

[2] CAMP and FRANCIS, 5th ed., p. 75.

there exists a potential reserve of about 70 billion tons of ore containing 25 to 50 per cent of iron in the Lake Superior region alone.

Blast-furnace Fuel and Reducing Agent.—In the earliest furnaces for the reduction of iron ores, wood charcoal was used as the fuel to obtain proper furnace temperatures; it also served directly or indirectly, through the formation of carbon monoxide, as the agent for reducing iron oxides of the ore to metallic iron. As the iron industry expanded and forests were depleted, other cheap and abundant blast-furnace fuels were developed. Charcoal was gradually displaced by anthracite grades of coal in the period, 1850–1880. Since that time both charcoal and anthracite have given way to coke made by the thermal decomposition, in the absence of air, of suitable grades of bituminous coal. Up until 1910, the bulk of metallurgical coke was made by the beehive process, but at the present time almost all of the coke used in the blast furnace is produced in by-product ovens (pages 44–48).

A good metallurgical coke should possess the following characteristics:[1]

1. *Composition.*—The volatile matter should not exceed 2 per cent; fixed carbon should be in the range 85 to 90 per cent; the ash should not exceed 13 per cent; but the sulfur and phosphorus contents, more important than the exact percentage of ash, should be kept as low as possible. Sulfur normally lies in the range 0.6 to 1.5 per cent and phosphorus should not exceed 0.018 to 0.04 per cent in a coke used for making bessemer iron (page 273).

2. *Physical Strength and Size.*—Coke for the iron blast furnace must be strong enough to support the solid burden in the stock column at the elevated temperatures obtained in the furnace. It should be free of dust and fines, and of such size as to promote the uniform flow of gases up through the solids in the stock column.

3. *Porosity.*—A porous open structure in the coke is desirable to increase its speed of combustion and its rate of reaction with carbon dioxide.

The physical properties of coke may be controlled to a certain extent by controlling the coking operation, but the production of a satisfactory metallurgical coke depends to a great extent upon the proper selection and blending of the bituminous coals that are charged into the by-product ovens.

Limestone.—Practically all iron ores contain silica in excess of that which can be held in combination by the basic oxides,

[1] CAMP and FRANCIS, 5th ed., p. 157. BOYLSTON, *op. cit.*, pp. 51–56.

CaO + MgO, present in the ores. Properly to flux the silica in the ore and coke, and furthermore to make a sufficiently basic slag to control the amounts of sulfur and silicon in the pig iron, limestone in the proper proportion is made a part of the blast-furnace charge (burden). In regular furnace operation, limestone loses its CO_2 about halfway down the stock column (page 269) and the remaining CaO becomes a constituent of the slag in the lower part of the furnace. Limestones suitable for the blast furnace should be low in silica, should be sized to particles from 1.5 to 6 in. in diameter, and normally should have compositions in the following ranges of percentages:

SiO_2	Fe	P	H_2O	Al_2O_3	CaO	MgO
1.2–3.43	0.3–0.6	0.006–0.033	0.6	0.7–0.86	51.4–53.9	0.7–1.7

Stone with the lowest phosphorus content is usually reserved for furnaces making bessemer iron.

Air.—To emphasize the importance of air as a raw material, one needs only to mention that the modern blast furnace must be supplied with about 8,500 lb. of air for every long ton of pig iron produced. Air must be supplied for the combustion of coke in the blast-furnace charge. It is forced in through tuyeres (page 264) near the bottom of the furnace at pressures ranging from 15 to 25 psi after being preheated in blast-furnace stoves[1] to temperatures ranging from 1000 to 1300°F. The influence of moisture in the hot blast on furnace operation recently has led to installations in some plants for controlling this factor.

Cooling Water.—The modern blast furnace requires much water for cooling the bosh (page 264) and the tuyères, and for scrubbing dust from blast-furnace gas. A furnace producing 1,000 tons of pig iron each 24 hours must be supplied with 6 to 8 million gallons of water per day.

Blast-furnace Design and Operation

The modern blast-furnace plant includes, in addition to the blast furnace proper, stoves for preheating the blast, blowing engines for supplying the blast, enormous storage bins for the solid raw materials, pumps and mains for cooling water, equipment

[1] Camp and Francis, 5th ed., pp. 253–256.

for cleaning blast-furnace gas, boilers for utilizing the blast-furnace gas not used in the stoves, blowing engines, slag cars and ladles for taking away the slag and pig iron as they are produced, a pig casting machine, and many other minor accessories. Such a plant will cost approximately 3 to 4 million dollars per furnace.

From an examination of Fig. 52, one may obtain a general idea of the layout of a blast-furnace plant. Figure 53 shows a cross

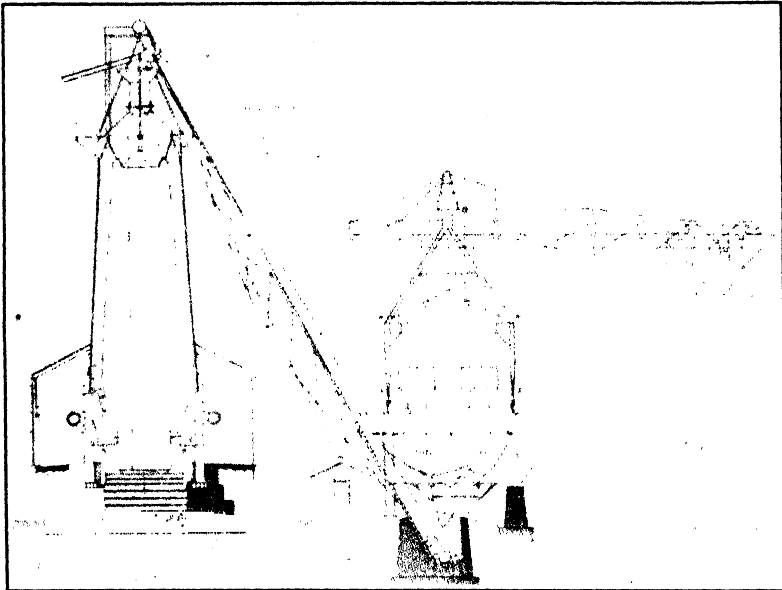


Fig. 52.—Section of blast furnace showing filling arrangement, bins and ore bridge.

section through a modern furnace in which its essential parts are indicated.[1] The refractory lining of the blast furnace is constructed of fire-clay bricks, the best grades of which are used in the walls of the crucible and bosh. The highest furnace temperatures are attained in the upper part of the crucible and the lower part of the bosh. Therefore, the firebrick in this region are protected by cooling plates built into the walls.

Outline of Blast-furnace Operation.—Once a blast furnace has been put in operation ("blown in") it produces pig iron, slag, and

[1] For a more detailed discussion of blast-furnace design see Camp and Francis, 5th ed., pp. 242–275; Sweetser, "Blast Furnace Practice," McGraw-Hill Book Company, Inc., New York (1938); Johnson, "Blast Furnace Construction," McGraw-Hill Book Company, Inc., New York (1917).

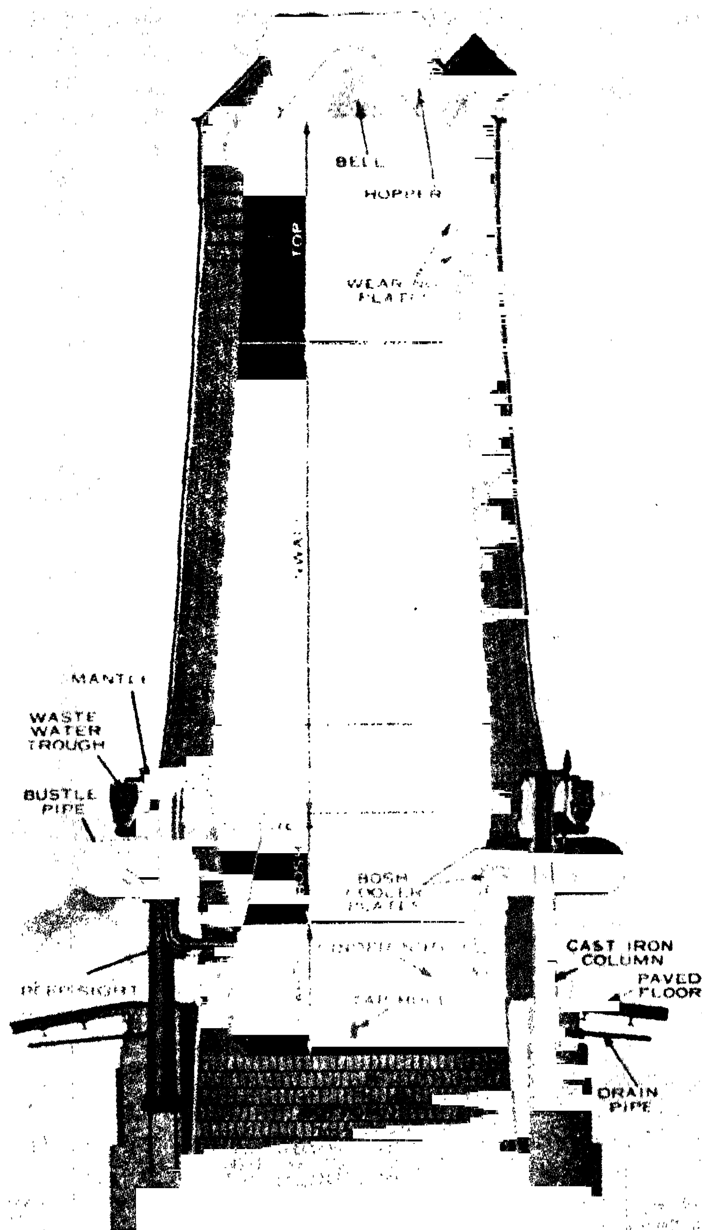


Fig. 53.—Design of a modern blast furnace. (*From "Modern Refractory Practice," Harbison-Walker Refractories Co.*)

blast-furnace gas by a continuous process. Alternate layers of ore, limestone, and coke, in the proper proportions for making a desired grade of pig iron, are charged at regular intervals into the top of the stock column through the charging bells. The "hot blast" of air preheated in the stoves is supplied through the tuyeres which are distributed about the circumference of the furnace just below the bosh zone. Molten pig iron covered by molten slag collects

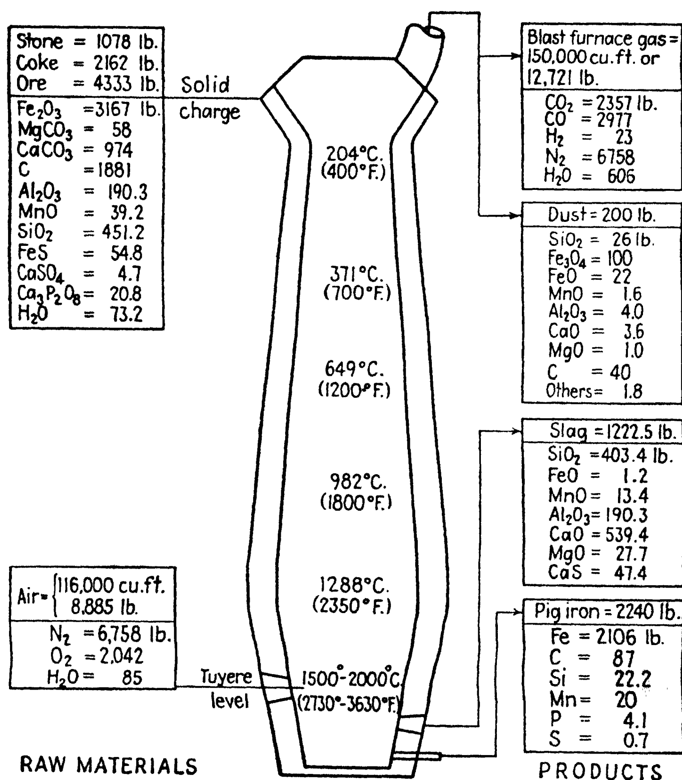


FIG. 54.—Blast-furnace raw materials, products, and temperatures.

in the crucible of the furnace. Every four or five hours pig iron is transferred from the furnace to the "hot-metal" ladles by opening the tap hole or "iron notch" and allowing the molten metal to flow through trenches (runners) to the ladles. In the ladles, pig iron is taken to the pig casting house or to the "hot-metal mixer" where it is stored and mixed with other casts to await its utilization in one of the steelmaking processes. Slag is tapped about every two hours by opening a tap hole ("cinder notch") located at a higher

level in the crucible. Slag or cinder is transferred to the slag dump in slag cars or "thimbles" or is led to the granulating pit (page 274). Blast-furnace gas (page 62) is produced continuously and leaves the top of the furnace through "offtakes" leading into larger mains called "downcomers" which take the gas to the cleaning equipment for the removal of dust, which normally varies from 7 to 30 grains per cubic foot. The dust content should not exceed 0.01 grain per cubic foot if the gas is to be used in gas engines, and the content should be in the range 0.2 to 1.0 grain per cubic foot when the gas is burned in blast-furnace stoves or under boilers. About 20 to 25 per cent of the gas is required for preheating the hot blast, 12 to 20 per cent is needed to operate the blowing engines, and the remainder is available for other uses about the plant.

Material Balance on the Blast Furnace.—Figure 54 gives, as an example, the amounts of the various raw materials required and the yield of products when a long ton of pig iron is produced. Approximate temperatures at various levels in the furnace also are given in Fig. 54. It should be emphasized that this is only an example and that the relative amounts of ore, coke, and stone in the charge (burden) will be adjusted by the blast-furnace operator and will depend upon the composition of his raw materials and the type of pig iron he wishes to produce. The calculation and regulation of the proportions of ore, flux (stone), and coke are called *burdening*. To control the operation of the furnace and the composition of the iron produced, the operator may, in addition to regulating the burden, vary the quantity and temperature of the hot blast. As will be learned from the following discussion, the temperatures that prevail in the bosh and the hearth, the slag basicity, and the slag viscosity have an important influence upon the composition of the pig iron.

Blast-furnace Reactions

The chemical reactions that take place in the blast furnace are of almost infinite variety and most of them are equilibrium reactions. The extent to which they may take place, therefore, depends upon the temperature; endothermic reactions becoming more and exothermic reactions becoming less complete as the temperature is raised.[1] Furthermore, most of the reactions occurring in the stock column involve solids and gases. The directions in which these

[1] McCutcheon, Seltz, and Warner, "General Chemistry," 3d ed., pp. 247–256, D. Van Nostrand Company, Inc., New York (1939). Getman and Daniels, "Outlines of Theoretical Chemistry," 6th ed., pp. 278–281, John

reactions take place, therefore, may be determined by the partial pressures[1] of the gases involved in the reaction as well as by the temperature. The rate at which these reactions between gases and solids occur also is important. Even though conditions of temperature and pressure favorable for a certain reaction are provided, the desired reaction may not be accomplished because the rate of reaction is slow. For reactions between gases and solids the extent of the solid surface is an important factor in determining the rate. For this reason, porous ores are more rapidly reduced than hard dense ones,[2] and a porous coke will react more rapidly with oxygen or carbon dioxide than a dense coke. To illustrate the importance of reaction rate, one may mention that in the top of the blast-furnace stock column temperatures and gas compositions prevail such that Fe_2O_3 could be reduced to solid iron. However, at these relatively low temperatures the rate of reaction of CO with the solid ore is so slow that very little if any reduction occurs.

Chemical Reactions in the Stock Column.—When the solid burden of ore, coke, and limestone enters the top of the stock column, it comes in contact with and receives heat from the hot gases that rise through the stock column. The first change involves the drying of the burden by driving off first adsorbed water and then combined water. In addition to drying, the following processes are encountered in the stock column:

1. Reduction of iron oxides by their interaction with carbon monoxide or with carbon directly.



$$3Fe_2O_3 + CO \rightleftharpoons 2Fe_3O_4 + CO_2 + 6{,}000 \text{ cal.} \qquad (1)$$



$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2 - 6{,}300 \text{ cal.} \qquad (2)$$



$$FeO + CO \rightleftharpoons Fe + CO_2 + 3{,}400 \text{ cal.} \qquad (3)$$



$$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2 + 3{,}900 \text{ cal.} \qquad (4)$$



$$3Fe_2O_3 + C \rightleftharpoons 2Fe_3O_4 + CO \qquad (5)$$



$$Fe_3O_4 + C \rightleftharpoons 3FeO + CO \qquad (6)$$



$$FeO + C \rightleftharpoons Fe + CO \qquad (7)$$



$$Fe_3O_4 + 4C \rightleftharpoons 3Fe + 4CO \qquad (8)$$

2. The deposition of carbon by CO or the "gasification" of carbon by CO_2 in the equilibrium reaction.



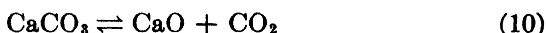
$$2CO \rightleftharpoons C + CO_2 \qquad (9)$$

Wiley & Sons, Inc., New York (1937). MacDougall, "Physical Chemistry," pp. 317–320, The Macmillan Company, New York (1936).

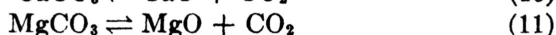
[1] See footnote on page 266.

[2] Joseph, *Trans. A.I.M.E.*, **120**, 72 (1936).

3. The thermal dissociation of calcium and magnesium carbonates.



$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad (10)$$



$$MgCO_3 \rightleftharpoons MgO + CO_2 \quad (11)$$

To make predictions concerning the possible direction of each of these reactions at various planes in the blast-furnace stock column, one would need to know the equilibrium conditions for each reaction, and the gas compositions, pressures, and temperatures that prevail at the various planes in the furnace. For some of the reactions,[1] precise equilibrium data are available and fair estimates may be made for the remainder. The best available data on gas compositions, pressures, and temperatures at various planes in the stock column of a furnace in regular operation were obtained by Kinney[2] on No. 4 furnace at the Carnegie-Illinois Steel Corp. South Works in Chicago. As an examination of this important paper will show, gas compositions, temperatures, etc., are by no means uniform across any plane in the furnace. However, for purposes of this discussion one may use the average integrated tem-

TABLE 52.—TEMPERATURES, PRESSURES, AND GAS COMPOSITIONS IN THE BLAST FURNACE

Plane	Distance from tuyères, ft.	Average integrated								
		Temperature, °C	Temperature °F.	% N_2	% H_2	% CO	% CO_2	Pressure atm.		$\frac{CO}{CO_2}$
								CO_2	Total	
Top of stock....	68.2	204	400	56.5	4.0	24.5	14.5	0.164	1.13	1.70
1	65.5	443	830	56.5	3.5	25.0	15.0	0.174	1.16	1.67
2	57.5	704	1300	56.5	3.3	25.0	15.0	0.200	1.33	1.67
3	46.5	854	1570	58.0	2.2	27.7	11.8	0.168	1.43	2.35
4	24.2	943	1730	60.0	1.0	34.5	5.5	0.094	1.71	6.30
Tuyère level....	0.0	...	....	66.5	1.5	32.0	0.0	0.000	2.00	

[1] For data on Eqs. (1) to (8) see Ralston, *U. S. Bur. Mines Bull.* 296; Schenck, "Physikalische Chemie der Eisenhüttenprozesse," Vol. I, pp. 141–154, Verlag Julius Springer, Berlin (1932).

For data on Eq. (9) see Maier, *U. S. Bur. Mines Bull.* 324; Kelley and Anderson, *U. S. Bur. Mines Bull.* 384.

For data on Eqs. (10) and (11) see Kelley and Anderson, *op. cit.*

[2] KINNEY, *U. S. Bur. Mines Tech. Paper* 442.

peratures, pressures, and gas compositions from Kinney's paper which are given in Table 52.

Realizing that local temperatures and gas compositions may vary enough from the average values given in Table 52 to alter conditions, one may at least draw the following general conclusions:

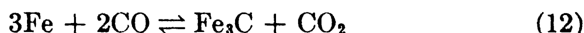
1. Calcium and magnesium carbonates can dissociate according to Eqs. (10) and (11) at plane 3 and at lower levels.

2. Carbon dioxide can gasify carbon [Eq. (9) going to the left] at planes 3 and 4. At plane 2 and above, carbon deposition can occur [Eq. (9) going to the right].

3. At any plane the ratio CO/CO_2 is great enough to reduce Fe_2O_3 to Fe_3O_4 [Eq. (1)].

4. From the top down to plane 2, conditions are probably favorable for the reduction of Fe_3O_4 to Fe. Owing to the low temperatures, this reaction is probably too slow to produce much iron.

5. Below plane 2, conditions are favorable for the reduction of Fe_3O_4 to FeO and to Fe containing some dissolved FeO [Eqs. (2) and (3)]. At plane 4, reduction can be quite complete and some carburization of the iron can begin.



$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2 \quad (12)$$



$$3Fe + C \rightleftharpoons Fe_3C \quad (13)$$

6. At plane 2 and above, CO in the gas has a higher reducing power than solid carbon and this together with the low temperatures makes direct reduction [Eqs. (5) to (8)] seem unlikely. At plane 3 and below, solid carbon has a higher reducing power than the CO in the gas, the temperatures are higher, and some direct reduction may be expected. However, the CO still can reduce the iron oxides in this region and, owing to the higher rate of the gas-solid reactions, it seems likely that a good portion of the reduction is accomplished by the gas.

7. The hot blast contains 79.2 per cent of nitrogen and other inert gases. These pass through the furnace essentially unchanged except for small amounts of nitrogen that react in the bosh zone to form cyanides. These cyanides apparently are decomposed at higher levels leading to the presence of traces of cyanogen, C_2N_2, in the blast-furnace gas. The large volume of inert nitrogen does serve a useful purpose in helping transfer the heat liberated in the combustion zone to the solid burden in the upper parts of the fur-

nace. However, it also makes unavoidable a considerable heat loss because of the sensible heat carried from the furnace.

8. Water vapor in the hot blast reacts with carbon, absorbing energy by the reaction



$$H_2O + C \rightleftharpoons CO + H_2 \qquad (14)$$

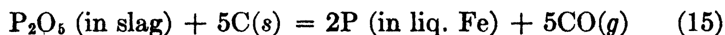
Some of this hydrogen may be used temporarily in the stock column for the reduction of iron oxides but it leaves the furnace largely as H_2 in the gas and thus represents an energy loss.

Chemical Reactions in the Bosh and Hearth.—The bosh and hearth of the blast furnace make up the smelting zone. As the materials of the charge move downward into the bosh zone with its higher temperatures and strongly reducing conditions, some oxides more stable than iron oxides are reduced; the gangue of the ore and coke combine with the basic oxides, CaO and MgO, from the stone to form a liquid slag over the molten pig iron in the hearth; spongy iron absorbs carbon [Eqs. (12) and (13)], melts, and rains down through the layer of liquid slag to join the layer of liquid pig iron in the bottom of the hearth or crucible.

One may summarize the behavior of the various elements in this smelting region as follows:

1. *Iron* is melted and carburized [Eq. (13)]. The liquid pig iron may contain from 3.0 to 5.0 per cent of carbon, but the usual range is 4.0 to 4.5 per cent. The iron also takes up manganese, silicon, sulfur, and phosphorus in varying amounts depending upon conditions as outlined below.

2. *Phosphorus* enters the furnace in the form of phosphates. Its principal source is the ore although small amounts normally are present in the coke and stone. Under the strongly reducing conditions that prevail in the hearth of the blast furnace, all of the phosphorus is reduced and enters the iron even though the slag is basic.



$$P_2O_5 \text{ (in slag)} + 5C(s) = 2P \text{ (in liq. Fe)} + 5CO(g) \qquad (15)$$

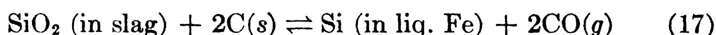


$$3Fe + P = Fe_3P \qquad (16)$$

To hold phosphorus in a basic slag, one must provide oxidizing conditions such as prevail in the basic open-hearth steelmaking process. Phosphorus in pig iron can be controlled only by controlling the phosphorus in the burden and this means principally the selection of an ore of sufficiently low phosphorus content. The acid bessemer and acid open-hearth steelmaking processes usually

require a pig iron containing 0.05 per cent or less of phosphorus (0.1 per cent P is certainly maximum). Ores that can be used to make such an iron are known as "bessemer ores."

3. *Silicon*, as free SiO_2 or combined with basic oxides as silicates, enters the furnace principally with the ore and coke. In the bosh zone the various silicates and alumina fuse to form the liquid slag, but under the reducing conditions and high temperature of the hearth some silica is reduced and enters the iron.



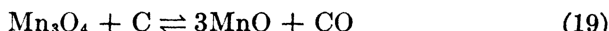
$$SiO_2 \text{ (in slag)} + 2C(s) \rightleftharpoons Si \text{ (in liq. Fe)} + 2CO(g) \quad (17)$$



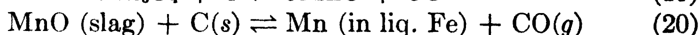
$$Fe + Si = FeSi \quad (18)$$

Reaction (17) is an endothermic equilibrium reaction and hence is favored by higher temperatures. The activity of SiO_2 in the slag decreases as the slag is made more basic because of compound formation with the basic oxides (especially with CaO). Evidently the amount of silicon in the iron may be controlled; as the temperature of the hearth is increased and as the slag is made less basic, the amount of silicon in the iron will be increased.

4. *Manganese* enters the furnace in the ore or in manganese-rich slags from the steel plant which often are made a part of the blast-furnace burden. In the smelting zone a good portion of the manganese is reduced and enters the liquid iron by the endothermic equilibrium reactions



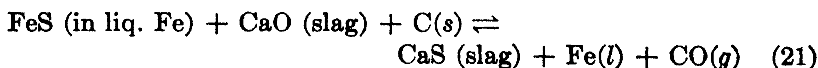
$$Mn_3O_4 + C \rightleftharpoons 3MnO + CO \quad (19)$$



$$MnO \text{ (slag)} + C(s) \rightleftharpoons Mn \text{ (in liq. Fe)} + CO(g) \quad (20)$$

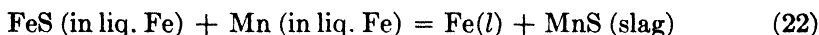
The higher the hearth temperature and the more basic the slag, the higher will be the Mn in the iron. In the normal operation of the blast furnace 50 to 75 per cent of the Mn in the charge is found in the pig iron. The amount of Mn in the iron also may be controlled by regulating the amount of Mn in the burden.

5. *Sulfur*.—The principal source of sulfur is the coke. By the time the charge has reached the bosh all sulfur compounds have been reduced to sulfides. As the iron melts, sulfur enters the iron as FeS. As the molten iron rains down through the slag, a considerable proportion of the sulfur may be transferred from the iron to the slag by the endothermic equilibrium reaction



$$FeS \text{ (in liq. Fe)} + CaO \text{ (slag)} + C(s) \rightleftharpoons CaS \text{ (slag)} + Fe(l) + CO(g) \quad (21)$$

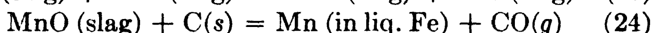
Desulfurization of the iron can be more complete the higher the hearth temperature and the more basic the slag. In ordinary practice, the reaction [Eq. (21)] is not sufficiently rapid to establish equilibrium. Hence, factors that help determine the speed of the reaction have an important influence upon the sulfur content of the iron. Slag viscosity,[1] which depends upon slag composition and temperature, is such a factor. An increase in the Mn content of the iron also seems to increase the speed of desulfurization, probably because reaction (21) is replaced by the more rapid reactions



$$FeS\ (\text{in liq. Fe}) + Mn\ (\text{in liq. Fe}) = Fe(l) + MnS\ (\text{slag}) \quad (22)$$



$$MnS\ (\text{slag}) + CaO\ (\text{slag}) = MnO\ (\text{slag}) + CaS\ (\text{slag}) \quad (23)$$



$$MnO\ (\text{slag}) + C(s) = Mn\ (\text{in liq. Fe}) + CO(g) \quad (24)$$

In general,[2] one may say that high temperatures, strongly basic slags, slags of low viscosities, and high Mn in the iron favor a low sulfur content in the iron.

6. *Aluminum, calcium,* and *magnesium,* which enter the furnace as oxides or compounds, are not reduced in the process and become constituents of the liquid slag in the smelting zone. CaO is the principal basic slag constituent. MgO, which is present in small amounts, is a minor basic constituent but it may have an important influence in determining slag viscosity.[3] Al_2O_3 plays a neutral or amphoteric role as a slag constituent but it also has an influence on slag viscosity. The chief acidic constituent of an iron- or steel-making slag is SiO_2 and the basicity of a slag is usually expressed by stating the ratio (per cent by weight)

$$\frac{CaO + MgO}{SiO_2}$$

In normal blast-furnace operation, this ratio has a value of about 1.5 for making basic open-hearth iron and a value of 1.3 to 1.4 for foundry iron.

Products of the Blast Furnace

In addition to its use for the production of various grades of pig iron, the iron blast furnace may be used to produce several

[1] Holbrook and Joseph, *Trans. A.I.M.E.* **120,** 99 (1936).

[2] For selected papers that give information on this important problem of desulfurization see Chipman and Li, *Trans. A.S.M.*, **25,** 435 (1937); Wentrup, *Iron Steel Inst., Carnegie Schol. Mem.*, **24,** 103 (1935); Maurer and Bischof, *J. Iron Steel Inst.*, **129,** 123 (1934).

[3] Holbrook and Joseph, *op. cit.*

TABLE 53.—CHIEF METALLIC PRODUCTS OF THE BLAST FURNACE*

Product	Maximum range, per cent of					Remarks
	Silicon	Sulphur	Phosphorus	Manganese	Total carbon	
Foundry pig irons	1.00– 4.00	0.04–0.10	0.10 –2.00	0.20–1.50	3.00–4.50	
Graded in steps of	0.50	0.01	0.20	0.20	Only the min. to be specified	
Tolerance, variation from per cent ordered	±0.25	Only max. to be specified	±0.15			
Most used grades:						
Northern foundry	1.75– 2.50	Under 0.05	0.15 –0.70	0.5 –1.00	4.0 –4.3	C not specified
Southern foundry	1.75– 2.25	Under 0.05	0.7 –0.9	0.40–0.75	3.75–4.1	C not specified
Malleable pig, standard	1.25– 2.25	Under 0.05	0.1 –0.19	0.4 –1.00	3.75–4.30	
Graded in steps of	0.25	....	0.05	0.20	Not to be specified	
Gray forge	1.20– 1.75	Under 0.05	0.1 –0.35	0.5 –1.00	4.15–4.40	C not specified
Puddling iron	0.75– 2.50	Under 0.05	0.1 –0.50	0.5 –1.00	4.10–4.40	Cr < 0.01
Acid pig, bessemer	1.00– 2.25	Under 0.045	0.04 –0.1	0.5 –1.00	4.15–4.40	C not specified
Open hearth	1.0 – 1.50	Under 0.045	Under 0.05	0.5 –1.50	4.15–4.40	C not specified
Basic pig, open hearth	Under 1.50	Under 0.05	0.11 –0.90	0.4 –2.0	4.10–4.40	C not specified
Bessemer or Thomas	0.5 – 1.00	Under 0.20	1.9 –2.5	1.5 –2.5	3.50–4.0	C not specified
Duplex iron	1.2 – 1.75	Under 0.060	0.7 –1.5	0.4 –0.90	4.00–4.20	
Special low phosphorus	Under 2.00	Under 0.035	Under 0.035	Under 2.00	....	C not specified
Spiegel (3 grades)	Under 1.25	0.03–0.05	0.14 –0.25	16–30	5.0 –6.5	C not specified
Silicospiegel	8.0 –15.00	Under 0.02	Under 0.15	15–20		
Ferromanganese	0.5 – 1.00	Under 0.05	0.2 –0.35	78–82	6.5 –7.5	C not specified
B. F. ferrosilicon, silvery pig	6.00–17.00	Under 0.05	0.10 –0.40	0.30–2.00	0.75–1.0	C not specified
Ferrophosphorus	1.5 – 1.75	Under 0.05	15–24	0.07–0.50	1.0 –2.0	C not specified

* From CAMP and FRANCIS, "The Making, Shaping, and Treating of Steel," 5th ed., The Carnegie-Illinois Steel Corp., Pittsburgh, Pa., (1940).

important ferroalloys that have extensive use in steelmaking. These together with the principal grades of pig iron are listed in Table 53.

The nonmetallic products of the blast furnace are gas and slag. The characteristics and uses of blast-furnace gas have already been described (page 266). Blast-furnace slag has found a variety of uses.[1] The greater proportion of it cannot be used except as ballast. For this purpose it is slow cooled on slag dumps or in slag pits and after weathering is crushed and screened to the desired size. Crushed slag also is an excellent aggregate for concrete work, being superior in some respects to crushed stone or gravel for this purpose. A considerable amount of granulated slag is used for making Portland cement (page 488). Slag is granulated by allowing the molten mass to flow into a pit partly filled with water. A small stream of water is forced against the underside of the slag stream as it leaves the runner and most of the slag is granulated before it falls into the water in the pit. A lightweight, fireproof, heat-insulating material is made by blowing air, or steam and air, into the slag as it solidifies. Finely crushed slag also finds some use in increasing the fire resistance of asphalt roofing and shingles.

PRODUCTION OF STEEL AND WROUGHT IRON

Pig iron (cast iron), when solidified, cannot be formed into desired shapes by the mechanical processes of forging (hammering or pressing) or rolling at any temperature. It must be formed by pouring the molten metal into a mold where it is allowed to solidify. The resulting casting is weak and brittle and, although its physical properties may be considerably improved by proper heat-treatment and alloying additions, cast iron is not suitable for the major portion of the industrial uses for ferrous materials.

Following the advent of the blast furnace as the most economical device for obtaining iron from its ores, a number of processes were devised to make a product sufficiently malleable and ductile to be formed into desired shapes by forging, rolling, or drawing at some temperature between room temperature and the melting point. Wrought iron, "ingot iron," "dead-soft" steel, plain carbon steels, and alloy steels are the products of these processes. The process for making wrought iron and the several processes for steelmaking will be discussed briefly in the following sections. The relative importance of these processes in the United States, which has

[1] SWEETSER, *op. cit.*, pp. 287–294.

produced more than half of the world supply, is indicated by the data in Table 54.

TABLE 54.—ANNUAL PRODUCTION OF STEEL AND WROUGHT IRON IN THE UNITED STATES*

Year	Wrought iron, long tons	Steel—long tons—ingots only					Total steel ingots + castings
		Bessemer	Open-hearth		Electric furnace	Crucible	
			Acid	Basic			
1870	1,291,000	37,500	1,339		None	?	68,750
1880	2,332,668	1,074,262	100,851		None	?	1,247,335
1890	2,920,367	3,688,871	513,232		None	?	4,277,071
1900	2,200,000	6,684,770	3,398,135		?	?	10,188,329
1910	1,740,156	9,354,437	782,805	14,858,353	50,821	107,671	26,094,919
1911	....	7,890,753	608,153	14,419,306	27,227	83,623	23,676,106
1920	1,377,566	8,778,107	759,102	30,926,393	346,956	70,536	42,132,934
1921	....	4,015,938	290,750	14,864,607	84,721	6,877	19,783,797
1929	475,049	7,091,680	576,393	46,644,206	532,392	5,762	56,433,473
1930	?	5,020,588	367,181	33,898,518	307,418	1,563	40,699,483
1931	?	3,011,394	194,388	21,986,933	235,376	831	25,445,501
1932	?	1,528,544	104,794	11,689,495	141,328	241	13,681,162
1933	?	2,428,799	195,495	19,972,805	299,808	399	23,232,347
1934	?	2,162,357	201,073	23,235,688	349,095	531	26,055,289
1935	?	2,835,031	248,512	30,334,442	521,818	642	34,092,594
1936	?	3,458,457	278,406	43,070,917	704,213	816	47,767,856
1937	?	3,449,927	333,473	45,719,507	814,310	934	50,318,151

* From CAMP and FRANCIS, "The Making, Shaping and Treating of Steel," 5th ed., The Carnegie-Illinois Steel Corp., Pittsburgh, Pa. (1940).

PRODUCTION OF WROUGHT IRON

Wrought iron[1] is a ferrous material, aggregated from a solidifying mass of pasty particles of highly refined metallic iron with which, without subsequent fusion, is incorporated a minutely and uniformly distributed quantity of slag. Wrought iron made from pig iron is very much like the product that was obtained by the direct reduction of ore in the forges and furnaces that preceded the blast furnace. In these furnaces, temperatures were not high enough to bring about either the solution of appreciable amounts of carbon in the iron or the fusion of the iron. Iron as a spongy plastic mass admixed with molten slag was the product of those early furnaces and its

[1] "Metals Handbook," 1939 ed., p. 457.

subsequent treatment was similar to that given wrought-iron "puddle balls" today.

Hand Puddling.—In the hand-puddling process, pig iron is charged into a reverberatory puddling furnace[1] on a hearth which has been prepared by "fettling" iron oxide into the sand bottoms and sides. After charging, heat is applied (melting period) to melt the pig iron. The molten metal covered with a thin layer of slag is then stirred with rabbles by the puddler (clearing period) to increase the rate of the refining reactions, which consist in this period chiefly in the oxidation of the silicon, most of the manganese, and a portion of the phosphorus. Next, by increasing the temperature and by the addition of mill scale or iron ore, the operator brings about carbon elimination (period of the high boil) leading to the formation of carbon monoxide, which burns as it bubbles up through the slag. As carbon is eliminated, the melting point of the iron is raised (page 315) and finally tiny particles of iron solidify and are gradually gathered into spongy balls and worked with the fluid slag. When the balls are sufficiently compact, they are removed from the furnace and passed between a toothed revolving cylinder and a section of a stationary cylinder to remove excess slag. The squeezed balls are then rolled into "muck bars" (3/4 to 1 in. thick and 2½ to 8 in. wide) and the muck bars later are piled, reheated, and rolled into billets, blooms, plates, and other suitable shapes. In the hand-puddling process, each puddle ball weighs 200 to 250 lb. and the output of a single furnace is about 2,800 lb. per day.

Mechanical Puddling Processes.—The desire to reduce the cost of making wrought iron to meet the competition from low-carbon steels and open-hearth irons, led to many attempts to invent processes whereby the same reactions that occurred in hand puddling could be carried out in mechanically operated equipment on larger masses of material. The most successful of the mechanical puddling processes[2] were the Roe process used by the Reading Iron Co. and the Ely process controlled by the American Chain Co.

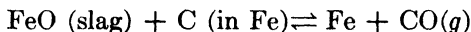
The Aston-Byers Process.[3]—The most significant improvement in methods for the large-scale production of wrought iron resulted from the work of Dr. James Aston and his associates at the A. M.

[1] Camp and Francis, 5th ed., pp. 305–307.

[2] Boylston, *op. cit.*, pp. 195–198.

[3] Aston and Story, "Wrought Iron," 2d ed., A. M. Byers Co. (1939) Aston, *Trans. A.I.M.E.*, **116**, 216 (1935).

Byers Co. In the Aston process, standard bessemer grade pig iron is melted in cupolas[1] (page 387), sulfur is reduced to below 0.03 per cent by the addition of soda ash, the molten metal is transferred to a 10-ton acid-lined bessemer converter (page 279) and blown to produce an iron of composition suitable for wrought iron. The blown metal is transferred in a ladle to the processing machine where it is poured at a controlled rate into an iron silicate slag which was separately prepared in an open-hearth furnace. The slag is held at a temperature of 2100 to 2200°F., which is 500 to 600°F. below the freezing point of the purified metal. As a consequence, iron particles solidify as they pass through the slag. A vigorous gas evolution accompanies the solidification because of the low solubility of gases in solid iron, and possibly also due to the reaction



$$FeO\ (slag) + C\ (in\ Fe) \rightleftharpoons Fe + CO(g)$$

which goes farther to the right as the temperature is dropped. This part of the process is known as the "shotting" operation. Under the prevailing conditions, the iron particles weld together to form an agglomerate cellular mass of iron admixed with slag which settles to the bottom of the "shotting thimble." After the excess slag is poured off, the sponge ball, weighing 6,000 to 8,000 lb., is dumped into a 900-ton press where the excess slag is removed and the mass is squeezed into a solid bloom for immediate rolling into billets and slabs by standard mill practice. The daily capacity of the Byers plant at Ambridge, Pa., is in excess of 800 tons.

Cement Steel and Crucible Steel

Wrought iron and other forms of commercially pure iron are too soft and ductile to serve many of the purposes for which it is desirable to use ferrous materials. To obtain the desired properties (strength, hardness, etc.), it is necessary to add the proper amounts of alloying elements, usually carbon, and subject the resulting alloy of iron (steel) to suitable heat-treatment, mechanical working, etc.

Prior to 1856, the year that marked the introduction of the bessemer process, the only methods for making steel were the cementation and crucible processes. Although steel made by these processes is insignificant in amount at present, it should be mentioned that the cementation process had much in common with the

[1] If molten bessemer grade pig iron is available directly from the blast furnace, this step in the process may be omitted.

present-day process for "pack carburizing" (page 338), and steelmaking in the high-frequency induction furnace (page 299) is a process practically identical with the crucible process.

Cement or Blister Steel.—By this process wrought iron, or other low-carbon irons or steels, were converted into higher carbon steels. The bars to be converted were packed in charcoal, sealed from air, and heated to a temperature of from 800 to 1100°C. (1470 to 2000°F.). About two days were required for the furnace to reach the full heat. The heat was then maintained 7 to 12 days longer, depending upon the product desired. Carbon penetrates the iron at the slow rate of about ⅛ in. every 24 hr. The saturation concentration of carbon in this temperature range varies from about 1.0 to 1.7 per cent, but the cementation process normally produced a product that was saturated with carbon only near the surface, the percentage of carbon decreasing toward the center of the bar. To obtain a more uniform distribution of carbon, it was common practice to sort and reheat the bars for hammering or rolling.

Steel made by this process was called "cement steel" because ferrite in the wrought iron was converted into cementite (iron carbide, page 315). As carbon migrates into wrought iron, it encounters slag particles rich in iron oxide, with which the carbon reacts to produce carbon monoxide (page 302). Near the surface, this reaction causes blisters to form, and for this reason the name "blister steel" also was applied to steel made by the cementation process.

Crucible Steel.—The lack of homogeneity in cement steel led Huntsman in 1742 to a rediscovery of the crucible process, a process that was certainly known and practiced by the early steelmakers of India, Damascus, and Toledo. Originally crucible steel was made by cutting into small pieces bars of cement steel, carefully selected to give the desired carbon content in the finished steel. The pieces were charged into a clay crucible large enough to hold about 50 lb. After a clay cover had been sealed on the crucible, it was placed in a coke fire until the contents were completely melted. The crucible was then taken from the furnace, the cover removed, the slag skimmed from the top of the melt, and the molten steel poured into a small cast-iron mold. This method gave a steel that was very homogeneous, free from slag and dirt, and much superior to cement steel. Later modifications of the process involved the use of crucibles of about 100-lb. capacity made of about equal parts of fire clay and graphite; the replacement of cement steel by wrought

iron or low-carbon steel with the proper addition of carbon and ferroalloys; and the use of gas-fired, regenerative-type furnaces in place of the coke fire. For the production of the finest steels, the crucible process held a dominant position for a period of almost 200 years. Recently, the crucible process has been largely replaced by the various electric furnace processes, which are capable of producing steel of equal or even better quality at lower cost.

The Bessemer Process

In the period 1870–1910, steel production showed a phenomenal increase due to the development of processes whereby steel for

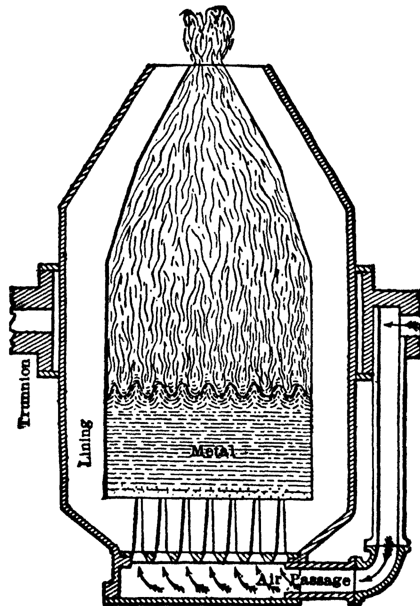


Fig. 55.—Bessemer converter purifying the metal. (*Lake.*)

structural and other uses could be produced from pig iron at low cost. The *bessemer* or *pneumatic* process was the earliest of these and held a dominant position throughout the above period. Owing to a combination of circumstances (page 287), the basic open-hearth process took the lead in about 1910 and has held that position ever since. In America, at the present time, approximately ten times as much steel is made by the open-hearth as by the bessemer process. Nevertheless, the bessemer process has held its own in recent years (Table 54, page 275) through demonstrating that it cannot be

excelled in producing steel for certain purposes. The process probably deserves more attention than it has received in the past.

Of all the processes for steelmaking, the bessemer is the simplest. It consists essentially of blowing cold air under pressure through molten pig iron in a refractory-lined vessel, called a converter, until such elements as silicon, manganese, and carbon have been removed by oxidation.

The Acid Bessemer Process.—In this process, which is the bessemer process used in America, the converter (Fig. 55) consists of an egg-shaped steel shell lined with first-class siliceous refractory. A common lining is composed of a course of splint brick next to the

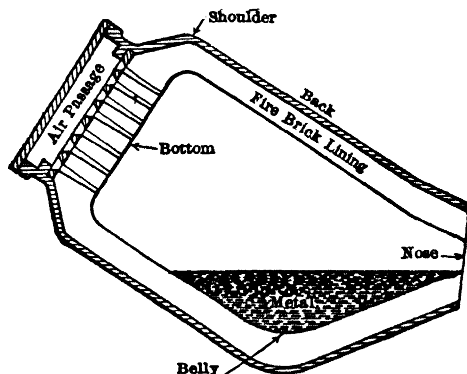


FIG. 56.—Bessemer converter tilted. (*Lake.*)

shell and an inner course about 12 in. thick of blocks of firestone, a highly siliceous sandstone, set in a mortar composed of "ball stuff" (5 parts crushed gannister and 1 part best quality fire clay). The bottom is detachable to facilitate relining, because it is subject to the greatest wear. To the bottom is attached a wind box with a space of an inch or so intervening between it and the bottom proper. About 20 firebrick cylinders, called tuyeres, lead from the wind box through the bottom lining to the interior of the converter. Each tuyère is about 7 in. in diameter and contains about twelve ½-in. tubes. The average life of a converter lining is about 800 heats; under good practice from 25 to 35 heats should be made on a single bottom. Converters vary in capacity from 10 to 25 tons.

The converter is mounted on trunnions attached to the side in such a manner that it may be tilted or in some cases turned entirely upside down. One of the trunnions is hollow and serves to connect the blast main to a pipe leading down the side of the converter

to the wind box. The nose of the vessel is formed by constricting the sides either concentrically or eccentrically. In either case the construction is such that, when the converter is tilted (Fig. 56), the charge may be contained without any of the tuyère holes being covered. This is necessary so that the blast may be turned off without metal running into the tuyeres.

Raw Materials for the Acid Bessemer.—The principal raw material is molten "bessemer grade" pig iron. Solid pig iron may be melted in a cupola furnace but is usually supplied directly from the blast furnace. Bessemer grade pig iron is characterized especially by its low phosphorus and sulfur contents because these elements are not eliminated in the bessemer process. However, it also is essential that the amounts of silicon and manganese in the iron be kept within fairly narrow limits. The following chemical specifications closely represent the present-day requirements on bessemer iron: carbon, 4.0 to 4.5 per cent; manganese, 0.70 per cent max.; phosphorus, 0.08 to 0.10 per cent; sulfur, 0.05 per cent max.; silicon, 1.00 to 1.75 per cent. Any iron ore from which a bessemer iron can be made is called a "bessemer ore." Since phosphorus cannot be removed in the blast furnace, this element must be present at low concentrations in a bessemer ore. Constancy of iron analysis as well as the actual composition is important. It also has been found advantageous to charge iron at a temperature of 2200 to 2350°F., and the more uniform this temperature is maintained from charge to charge, the smoother will be the bessemer operation. Improvements in the constancy of both iron composition and iron temperature are obtained by the use of the "hot-metal mixer" which is described below.

A dependable supply of air at a pressure that may be controlled between 10 and 25 psi must also be considered an important raw material. The lower pressure is just about sufficient to keep the metal out of the tuyères when the converter is in an upright position. The use of other minor but essential raw materials such as steel scrap, spiegel, ferromanganese, and ferrosilicon, will be described in following paragraphs.

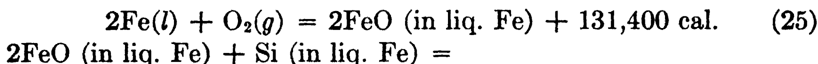
The Hot-metal Mixer.—The "hot-metal mixer"[1] serves primarily as a storage place for "hot metal" (molten pig iron) from the blast furnace and is almost indispensable to any modern steelmaking plant. A mixer is a large cylindrical vessel con-

[1] Invented by Captain W. R. Jones in 1889 at the Edgar Thomson Plant of the Carnegie Steel Co., Braddock, Pa.

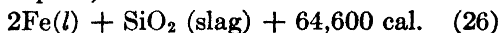
structed of a steel shell lined with silica brick or a good grade of firebrick. The vessel is set on racers and rollers so that it may be tilted to pour metal into ladles for transfer to the bessemer converters or open-hearth furnaces. Metal from the blast furnace is poured into the mixer through an opening at one end of the top. Most modern mixers will hold 1,200 to 1,300 tons of metal. The benefits derived from the mixer are (1) conservation of heat in the pig iron, keeping the metal molten; (2) delivery to the converter or open hearth of iron more uniform, both chemically and physically, than the iron in separate blast-furnace casts; (3) casts slightly high or low in analysis or temperature may be mixed with other iron of correct analysis and temperature, thus minimizing offcasts; (4) some reduction in the sulfur content of the metal may be accomplished in the mixer under certain conditions.[1] The iron temperature in a mixer is usually held at 2200 to 2400°F.

The Bessemer "Blow."—In making a heat of bessemer steel, the converter is turned on its side and a charge of molten pig iron is poured in from a ladle. The charge will form a layer of metal 18 to 20 in. deep when the converter is turned to the upright position. Before turning up the converter, the blast is turned on. Although more than 5,000 cu. ft. of air per min. pass through the shallow layer of metal, practically no oxygen escapes uncombined. This high rate of absorption of oxygen is due to the fact that the blast assumes the form of a spray of fine bubbles.

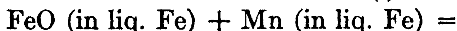
During the first period of the blow, silicon and then manganese are oxidized, probably by a mechanism that involves oxidation of iron to FeO by the blast and reaction of the dissolved FeO with the Si and Mn.

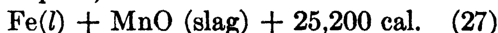


$$2Fe(l) + O_2(g) = 2FeO \text{ (in liq. Fe)} + 131{,}400 \text{ cal.} \quad (25)$$



$$2FeO \text{ (in liq. Fe)} + Si \text{ (in liq. Fe)} = 2Fe(l) + SiO_2 \text{ (slag)} + 64{,}600 \text{ cal.} \quad (26)$$





$$FeO \text{ (in liq. Fe)} + Mn \text{ (in liq. Fe)} = Fe(l) + MnO \text{ (slag)} + 25{,}200 \text{ cal.} \quad (27)$$

Thus the oxidation of a gram molecular weight (one mole) of silicon results in the evolution of 196,000 cal. of heat and the oxidation of a mole of manganese liberates 90,900 cal. Inasmuch as silicon is present in considerable amounts, it is easy to understand the reason for calling this element the principal fuel in the bessemer process.

[1] WENTRUP, *op. cit.*

During this period, FeO is produced in excess of that which can dissolve in the liquid iron and that needed for the oxidation of silicon and manganese. This excess FeO becomes a part of the slag where it joins the MnO in forming more or less stable compounds with the silica, of which the following may be considered typical:



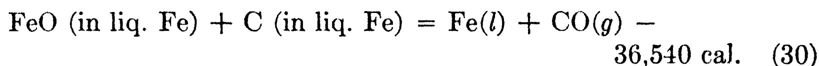
$$FeO\ (slag) + SiO_2\ (slag) = FeSiO_3\ (slag) + 9{,}300\ cal. \quad (28)$$



$$MnO\ (slag) + SiO_2\ (slag) = MnSiO_3\ (slag) + 5{,}400\ cal. \quad (29)$$

These exothermic reactions [Eqs. (25) to (29)] of the first period of the blow supply heat faster than it is lost by radiation and in the exit gases and, as a consequence, the temperature of the iron increases during this period. At the beginning of the blow, a shower of sparks is emitted from the mouth of the converter. Next a stream of dense brown fumes pours forth, to be followed shortly by a dull-red, short pointed flame. About 5 or 6 min. after the beginning of the blow, the flame becomes a short luminous one, marking the end of the first period in which most of the silicon and manganese has been eliminated and the oxidation of carbon has begun.

In the second period, the luminous flame increases in length to 30 ft. or more as carbon is rapidly oxidized.



$$FeO\ (in\ liq.\ Fe) + C\ (in\ liq.\ Fe) = Fe(l) + CO(g) - 36{,}540\ cal. \quad (30)$$

Toward the end of the blow, the flame begins to die away, but before it disappears entirely the converter is turned down and the blowing is stopped. The total blowing time will vary between 10 and

TABLE 55.—A TYPICAL ACID BESSEMER BLOW*

Element	Initial charge, %	Composition after various times during blow				
		2 min.	3 min. 30 sec.	6 min.	8 min. 10 sec.	10 min.
Carbon	4.30	3.90	3.75	2.10	0.60	0.03
Silicon	1.25	0.70	0.38	0.03	0.03	0.005
Manganese	0.40	0.10	0.04	0.03	0.01	0.01
Phosphorus	0.085	0.088	0.090	0.092	0.094	0.096
Sulfur	0.035	0.035	0.036	0.037	0.038	0.039

* From HENNING, *Trans. Amer. Inst. Min. Met. Engrs.*, **116**, 137 (1935).

20 min., depending upon the temperature and composition of the iron, and the practice that has been adopted as standard in the bessemer plant for producing a specific grade of steel.

The course of the refining process during a blow in the converter is indicated in Table 55.

As Table 55 indicates, phosphorus and sulfur are not eliminated in the acid bessemer process. These elements actually increase slightly in concentration due to a loss of 8 to 9 per cent of the weight of the charge during the blow. Henning[1] estimates the bessemer losses as follows:

	Per Cent of Charge
Carbon burned	4.3
Silicon burned	1.25
Manganese burned	0.40
Iron in slag and pellets	1.50
Material ejected and volatilized	1.00
Total loss	8.45

Temperature control during the blow is important and the operator has several means at his disposal to exercise some control over this variable. If the temperature is too low, ferrosilicon may be added or the converter may be turned to expose a few tuyères. The combustion of CO over the bath will generate heat, raising the temperature of the converter and the metal bath. If the temperature is too high, the vessel may be tilted and allowed to cool by radiation, or cold steel scrap may be added if the blow is not too far advanced.

Deoxidation, Recarburization, and Alloying Additions.—With careful control it is possible to stop the blow when the steel contains the required amount of carbon. It is a more common practice, however, to continue the blow until almost all of the carbon has been removed and then make an addition in the ladle to meet the carbon specification. At the end of the blow, the metal, which has been exposed to strongly oxidizing conditions, contains a considerable amount of FeO. If the oxide were allowed to remain, the steel would be brittle and otherwise defective. The removal of FeO from steel is referred to as *deoxidation* (page 301) and, although many other substances (page 302) might be used, manga-

[1] HENNING, *Trans. A.I.M.E.*, **116**, 137 (1935).

nese in the form of ferromanganese or spiegeleisen is most commonly used in bessemer practice.[1]



$$\text{FeO (in liq. Fe)} + \text{Mn (in liq. Fe)} \rightleftharpoons \text{Fe}(l) + \text{MnO (slag)} \quad (31)$$

Since the bulk of bessemer steel produced today is of low-carbon grades (carbon under 0.20 per cent) and most ferromanganese and spiegel contain 6 to 7 per cent of carbon, it is usually possible to accomplish deoxidation and recarburization simultaneously by the addition of suitable grades of ferromanganese and spiegel. For the higher carbon grades, the addition of molten pig iron is favored over anthracite coal or coke as the recarburizer.

Additions of ferromanganese and other recarburizers are usually made to the ladle (page 305) after the heat has been transferred from the converter to the ladle. Copper additions for making copper-bearing steels (page 358) are made in the converter. To meet specifications for the high-sulfur screw steels, present practice favors the addition of iron pyrites to the converter rather than the addition of sulfur to the ladle. In making semikilled or killed steel (page 303) other deoxidizers, usually shot aluminum or fine 50 per cent ferrosilicon, may be added to the liquid steel in the molds (page 306).

After proper additions to the steel in the ladle and possibly holding for some time in the ladle, the steel is "teemed" into ingot molds through a nozzle in the bottom of the ladle. Since the ingot-making stages in steel manufacture are very similar for various processes, teeming will be discussed in a later section (page 304).

Bessemer Steel Products.—The bulk of the steel produced today by the acid bessemer process goes into screw steel, sheet steel, tin plate, wire, skelp for welded pipe, and bars for bolts, nuts, concrete reinforcing, track spikes, and small structural and special shapes. In comparison with similar grades of open-hearth steel, greater machinability, stiffness, and weldability are claimed for bessemer steel.

The Basic Bessemer or Thomas Process.—This process is applicable to making steel from pig iron which contains more than 1.5 per cent of phosphorus (see Table 53, page 273). Since American ores do not produce pig iron that high in phosphorus, this

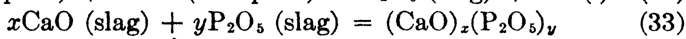
[1] It is interesting to note that in the early attempts to use the bessemer process on low-manganese iron, the steel almost invariably was brittle when hot. The method seemed doomed to failure until the beneficial effect of adding manganese after blowing was recognized.

process is not used in this country. In England and on the continent of Europe, it has been an important steelmaking process since about 1885. The Thomas converter is similar to the acid bessemer except that it is lined with a mixture of tar and burned dolomite or other basic refractory.

After charging the molten pig iron, lime is added to make a basic slag. During the first part of the blow, silicon is rapidly and completely eliminated, manganese is slowly and only partly removed, and, following the silicon elimination, carbon is rapidly oxidized. The period following carbon elimination is known as the "afterblow." In this period, phosphorus is oxidized and combines with CaO to form calcium phosphates in the basic slag.



$$2P \text{ (in liq. Fe)} + 5FeO \text{ (in liq. Fe)} \rightleftharpoons P_2O_5 \text{ (slag)} + 5Fe(l) \quad (32)$$



$$xCaO \text{ (slag)} + yP_2O_5 \text{ (slag)} = (CaO)_x(P_2O_5)_y \quad (33)$$

The afterblow requires 2 to 4 min., depending upon the amount of phosphorus in the iron and other conditions. The basic bessemer process also has the advantage of controlling sulfur, about half of the sulfur present in the iron being eliminated in the blow.

The Open-hearth Process

In the period 1860–1870, William Siemens applied the regenerative principle, which he had invented, to the construction of furnaces for making steel; first by melting steel scrap and later by melting pig iron and oxidizing the impurities by additions of iron ore on a hearth above which preheated producer gas was burned with preheated air to obtain suitable temperatures. Regenerative furnaces are equipped on either end with chambers partly filled with brickwork called "checkers."[1] During one half cycle, the hot combustion products pass from the furnace to the checkers, transferring much of their sensible heat (page 74) to the brickwork before passing to other heat exchangers and the stack. During the next half cycle, the air for combustion and sometimes the fuel gas are brought to the furnace through these checkers, taking up heat from the brickwork. On this half cycle, the hot combustion products are used to heat the checkers on the other end of the furnace.

The hearth of the Siemens furnace, constructed of acid brick covered with sintered sand, was very much like the hearth of modern acid open-hearth furnaces. Later, the important basic

[1] Danforth, *Proc. Nineteenth Open Hearth Conference, A.I.M.E.* (1936), pp. 46–59. Quigley, *Yearbook A.I.S.I.* (1923), pp. 382–410.

open-hearth process was introduced by constructing hearths of magnesite brick covered with a layer of burned dolomite or magnesite. The Martin brothers modified Siemens' process by melting pig iron with steel scrap instead of with iron ore. Because the modern open-hearth process utilizes steel scrap, pig iron, and iron ore, it is frequently called the Siemens-Martin process.

The Basic Open-hearth Process

As may be noted from Table 54 (page 275), 85 to 90 per cent of the steel produced in the United States is made by the basic open-hearth process. This process is so extensively used because (1) the bulk of American ores yield a pig iron that can most economically be converted into desirable grades of steel in the basic open hearth. (2) The ratio of pig iron to scrap in the charge may be varied over wide limits and hence is adjustable depending upon the relative prices of pig iron and scrap; no other steelmaking process permits so great a latitude in the character of its raw materials. (3) The process affords better control over both temperature and steelmaking reactions than is possible in the bessemer process.

The Basic Open-hearth Furnace.—The furnace proper is a rectangular brick structure, supported on the sides and ends by steel buckstays which are bound together at their tops by rods and stays. Furnaces have been built with hearth capacities ranging all the way from 15 to 350 tons, with 100 tons as the most common size. The over-all outside dimensions of the 100-ton furnace will be about 80 ft. in length and 20 to 22 ft. in width, with a hearth depth of 24 to 30 in. The various parts of the stationary furnace and the details of the construction[1] are well illustrated in Fig. 57. The various types of refractories[2] (page 109) used in the furnace also are indicated in the figure. Most modern furnaces have insulation[3] on the roof, side walls, and checkers to conserve heat and to permit better control over combustion and furnace atmospheres.

Some open-hearth furnaces, especially those used in the duplex process (page 301) and in some steel foundries, are set on rollers so

[1] For a detailed description of furnaces recently constructed by the Inland Steel Co. see Hutchinson, *Proc. Twentieth Open-hearth Conference, A.I.M.E.* (1937), p. 28.

[2] Many practical open-hearth refractory problems are discussed in *Proc. Nineteenth Open-hearth Conference, A.I.M.E.* (1936), pp. 85–117.

[3] Cone, *Proc. Nineteenth Open-hearth Conference, A.I.M.E.* (1936), pp 91–107.

that they may be tilted to pour slag or molten metal from the furnace. These tilting open hearths usually are designed to rotate about a center on a line joining the ports so that the flame may be kept on when the furnace is tilted. The checker chambers are located under the charging floor in front of the furnace.

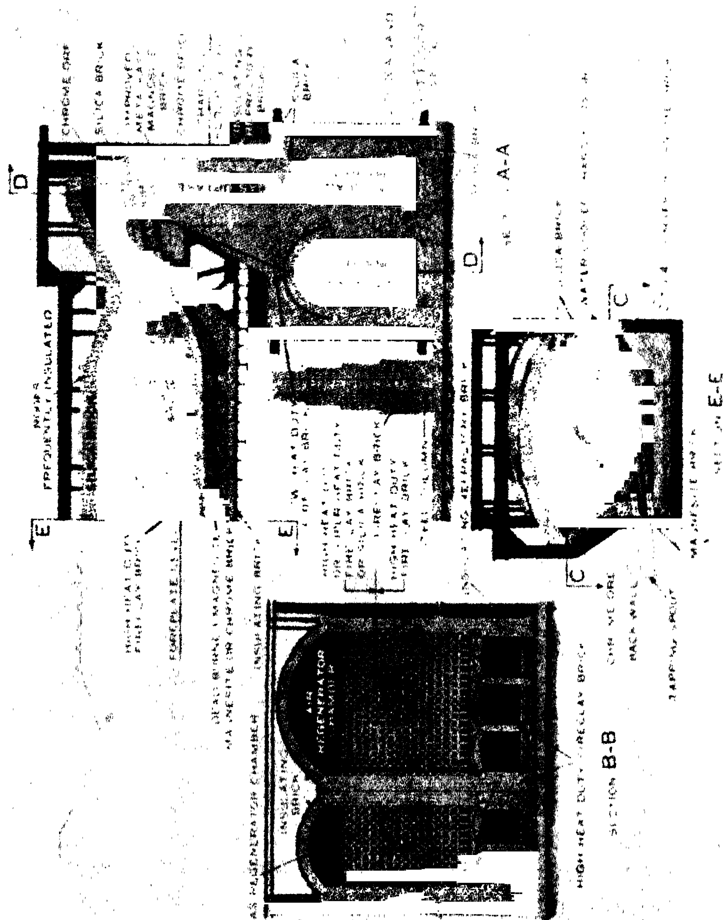


FIG. 57.—The basic open-hearth furnace. (From "Modern Refractory Practice," The Harbison-Walker Refractories Co.)

The basic bottoms of furnaces, if properly constructed and carefully patched between heats, have a long life. Many bottoms have been in service for 20 to 30 years. The roof, end walls, and checkers need frequent repair and occasional rebuilding. Checkers,

to function properly, must be cleaned every 75 to 600 heats, depending upon the type of fuel used.

The furnace proper is only a part of the modern open-hearth plant. If producer gas is used as a fuel, gas producers must be built adjacent to the open hearths. If other fuels are used, equipment for their storage and delivery to the furnaces must be provided. Stockyards equipped with cranes for filling charging boxes; cars and locomotives for taking the boxes to the charging floor; charging machines for emptying charging boxes in the furnace; hot-metal mixers for storing molten pig iron; cranes and ladles for transferring hot metal from the mixer to the furnaces; cranes, slag thimbles, teeming ladles, and a steady supply of ingot molds on the tapping floor, and a number of minor accessories are required in the modern plant. Furthermore, it is usually equipped with waste-heat boilers and heat exchangers to extract sensible heat from the furnace gases between the checkers and the stack; and instruments for the automatic control of fuel-air ratios, furnace temperatures and pressures, furnace reversals, etc., are coming into more common use.

Open-hearth Fuels.—Fuel costs account for about 4.0 per cent of the cost of making steel in the open hearth. In addition to the actual cost per B.t.u., other factors must be considered in the selection of the fuel for open-hearth furnaces:

1. The temperature attainable with the fuel.

2. The ease with which proper direction may be given to the flame. This is important in determining the life of refractories in the roof and end walls, and in controlling the oxidation of the bath.

3. The sulfur content of the fuel has an important bearing in determining whether sulfur will be "picked up" or eliminated in the open-hearth process.

4. The luminosity of the flame produced by the fuel. Heat is transferred from the flame to the bath (slag and molten metal) by convection, by radiation from the roof and walls, and by radiation from incandescent particles in the flame if it is luminous.

5. The "cleanliness" of the fuel, *i.e.*, the amount of slag, dirt, etc., that is carried over into the slag pockets and checkers. These must be cleaned every 75 to 125 heats when powdered coal is used and only every 300 to 600 heats when natural gas or coke-oven gas is used.

6. The design of the furnaces in the plant must be considered. There is a best end wall and port construction for each fuel and it

might be unprofitable to change to a new fuel, which otherwise would be very desirable, because of the changes that would be necessary in the furnaces.

The fuels used in open-hearth furnaces are natural gas, coke-oven gas, producer gas, pulverized coal, fuel oil, tar, and blast-furnace gas. These fuels were described in Chap. II. Natural gas and fuel oil are very desirable fuels; they are generally low in sulfur, burn with a luminous flame, and are clean fuels. Coke-oven gas and coke-oven tar give flames of good luminosity but are usually considerably higher in sulfur and are not so clean as natural gas.

Producer gas and blast-furnace gas burn with a fairly non-luminous flame, usually are moderately high in sulfur, and are moderately clean. Coal, pulverized so that 85 per cent passes a 100-mesh sieve and 80 per cent passes 200-mesh, gives a rapid burning, very luminous flame. It is rarely used, however, because of the hazards connected with its grinding and storage and because it so rapidly fouls the checkers and is abrasive on refractories.

The large integrated iron and steel plant produces blast-furnace gas, coke-oven gas, and coke-oven tar. As a consequence, one usually finds the large open-hearth plants using one or more of the following fuels or combinations of fuels: coke-oven gas, coke-oven gas and tar, or coke-oven gas and blast-furnace gas. Blast-furnace gas is never used alone.

Producer gas and mixtures of blast-furnace gas with coke-oven gas may be preheated in checkers before burning. The other fuels, higher in hydrocarbon content, cannot be preheated in checkers without decomposition leading to the deposition of carbon and tar which clogs the checkers.

Basic Open-hearth Raw Materials.—The principal raw materials are steel scrap, solid or molten pig iron, iron ore or mill scale, and limestone. Other minor raw materials are burnt lime, fluospar, and dolomite as slag additions; anthracite coal, coke, or wash metal[1] for recarburizing; ferroalloys for deoxidation (page 304) and meeting specifications on alloying constituents; and a considerable variety of refractories for the maintenance and repair of ladles and furnaces.

The usual range of composition for basic open-hearth irons is given in Table 53. Most open-hearth operators[2] want an iron with

[1] Wash metal is made by removing almost all metalloids except carbon from pig iron.

[2] *Proc. Twentieth Open-hearth Conference, A.I.M.E.* (1937).

silicon between 0.80 and 1.20 per cent, sulfur as low as possible, and manganese fairly high. The constancy of the composition of the pig iron supplied to the open hearth is generally held to be more important than the actual analysis. Although steel can be and is made with cold pig iron in the charge, the bulk of open-hearth steel is made from liquid pig iron direct from the blast furnace. The latter practice conserves the sensible heat in the hot metal and decreases the time required per heat.

Steel scrap should be selected with care to avoid contamination from undesired alloying elements and to regulate the time required for melting and the extent of oxidation of the scrap during melting. Most operators prefer a mixture of light and heavy scrap. Heavy scrap melts more slowly but light scrap becomes more highly oxidized because more surface is exposed to the oxidizing gases. Iron oxide in the form of crushed hard ore or briquetted mill scale is preferred over fine ore for most purposes.

The Charging and Melting Periods.—Ordinarily in charging a basic open-hearth furnace to make a heat of steel, limestone in proper amount is placed on the hearth first. This is followed by the proper amount of iron ore, and then by scrap. Some cold pig iron is frequently charged on top of the scrap. After the scrap has partly melted and the furnace has become well heated (1 to 2 hr. after the scrap has been charged), hot metal is brought from the mixer in a ladle and poured into the furnace through a spout inserted in one of the charging doors.

During the period between the charging of the scrap and the hot metal addition, the scrap is subject to considerable oxidation by reaction with oxygen, water vapor, and carbon dioxide in the furnace gases. During this period the calcination of limestone also begins and the carbon dioxide from this source causes further oxidation of the metal. As a consequence, when the hot metal is added there is a rather violent reaction between the Si, Mn, P, and some of the carbon in the hot metal and the iron oxide on the oxidized scrap leading to the production of a slag. This first slag is much less basic than the slag that covers the bath later in the heat. It is high in SiO_2, MnO, and FeO and contains roughly half of the phosphorus that was present in the charge. This slag is very viscous, and owing to entrapped CO from carbon oxidation the slag rises and runs off through a hole above the normal slag line in the back of the furnace. It is called a "runoff slag"; the time during which it is formed is often called the "runoff period."

The elimination of much of the silicon and some of the phosphorus in the runoff slag allows the operator to work with a smaller slag volume and a less basic slag during the remainder of the heat. Unfortunately much of the manganese and considerable iron also leave the furnace in the slag. Some of the iron and manganese is recovered by charging at least a portion of the slag into the blast furnace. In stationary furnaces it is impossible to produce a runoff slag unless hot metal makes up about 40 to 50 per cent of the metallic charge. However, in tilting furnaces, this first slag can be removed from the furnace with any type of charge.

Period of the Lime Boil.—Following the runoff period, the temperature on the bottom of the hearth reaches that required for the rapid calcination of the limestone and for completing the melting of the scrap. During this period there is violent agitation of the bath by the evolved CO_2, and the CaO, no longer held on the bottom by the scrap, comes up through the bath and becomes a part of the slag. Part of the CO_2 reacts with iron in the bath.



$$CO_2(g) + Fe(l) \rightleftharpoons FeO \text{ (in liq. Fe)} + CO(g) \qquad (34)$$

Shaping Up the Heat.—When the lime is up and the completely liquid bath is covered with a layer of slag, one has the first opportunity to obtain fairly representative samples of metal and slag for test and analysis. The operator then estimates the proper additions of ore and stone for "shaping up the heat" on a basis of (1) the preliminary tests on the slag and metal, (2) the grade of steel being made and the carbon drop desired before tapping, and (3) the amount of runoff slag produced.

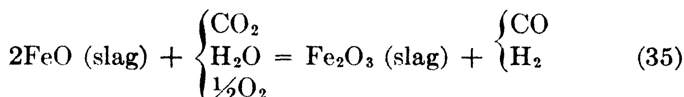
The Refining Period.—The period during which ore and stone additions are made is often called the refining period. Silicon was eliminated early in the heat, some residual phosphorus, manganese, and sulfur still are present, but the principal reaction during the refining period is the oxidation of carbon. During this period, the oxidizing power, basicity and viscosity of the slag, and the furnace temperature are adjusted to control the rate of carbon drop, and to control the distribution of sulfur, phosphorus, and manganese between metal and slag.

The oxidizing power of the slag depends upon the concentration of FeO plus Fe_2O_3, and upon the basicity of the slag which usually is expressed by giving the ratio of basic to acidic oxides in the slag. For a given concentration of FeO plus Fe_2O_3 in the slag, there will be a certain basicity at which the slag will have a maximum oxidiz-

ing power. In more acid slags, the oxidizing power decreases because FeO combines with SiO_2. In more basic slags, the oxidizing power is decreased by Fe_2O_3 combining with CaO. The oxidizing power of a slag is increased with a rise in temperature.

The viscosity of the slag is important because this property influences the rate at which iron oxide is transferred from the slag to the bath and the rate of the other reactions, which involve the distribution of phosphorus, sulfur, and manganese between metal and slag. Slag viscosities increase with decreasing temperatures and with increased basicity. Suspended rather than dissolved CaO increases slag viscosity but the addition of fluospar will decrease slag viscosity without appreciably influencing its basicity.

The available oxygen in the slag may be increased by ore additions or by oxidation of the slag by the furnace gases.



$$2FeO\ (\text{slag}) + \begin{Bmatrix} CO_2 \\ H_2O \\ \tfrac{1}{2}O_2 \end{Bmatrix} = Fe_2O_3\ (\text{slag}) + \begin{Bmatrix} CO \\ H_2 \end{Bmatrix} \quad (35)$$

In the refining reactions, FeO and Fe_2O_3 are transferred to the metal-slag interface by diffusion and convection, processes that are the more rapid the lower the slag viscosity. At the slag-metal interface

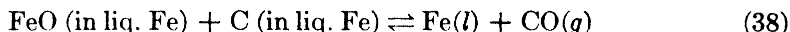


$$FeO\ (\text{slag}) \rightleftharpoons FeO\ (\text{in liq. Fe}) \quad (36)$$

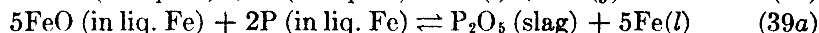


$$Fe_2O_3\ (\text{slag}) + Fe(l) \rightleftharpoons 3FeO\ (\text{in liq. Fe}) \quad (37)$$

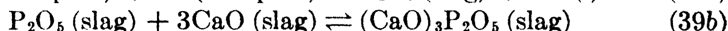
FeO in the metal bath then reacts with carbon, phosphorus, and manganese as indicated by the following equations:



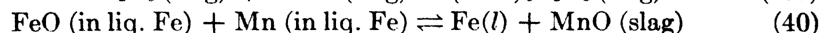
$$FeO\ (\text{in liq. Fe}) + C\ (\text{in liq. Fe}) \rightleftharpoons Fe(l) + CO(g) \quad (38)$$



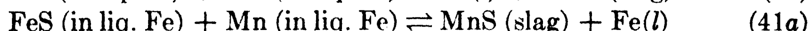
$$5FeO\ (\text{in liq. Fe}) + 2P\ (\text{in liq. Fe}) \rightleftharpoons P_2O_5\ (\text{slag}) + 5Fe(l) \quad (39a)$$



$$P_2O_5\ (\text{slag}) + 3CaO\ (\text{slag}) \rightleftharpoons (CaO)_3P_2O_5\ (\text{slag}) \quad (39b)$$



$$FeO\ (\text{in liq. Fe}) + Mn\ (\text{in liq. Fe}) \rightleftharpoons Fe(l) + MnO\ (\text{slag}) \quad (40)$$



$$FeS\ (\text{in liq. Fe}) + Mn\ (\text{in liq. Fe}) \rightleftharpoons MnS\ (\text{slag}) + Fe(l) \quad (41a)$$



$$MnS\ (\text{slag}) + CaO\ (\text{slag}) \rightleftharpoons MnO\ (\text{slag}) + CaS\ (\text{slag}) \quad (41b)$$

If the principles of physical chemistry are applied to the above reactions, one may draw the following conclusions:

1. The higher the degree of oxidation of the metal bath, the more rapidly carbon will be eliminated and the lower the residual carbon at the end of the heat. The basicity of the slag is of importance only inasmuch as it influences the availability of iron oxides in the

slag and as it influences, through its effect on viscosity, the rate of transfer of oxygen from slag to bath.

2. A highly oxidized bath and a very basic slag favor phosphorus elimination.

3. A low degree of oxidation of the bath and a basic slag favor a high residual manganese in the bath.

4. High residual manganese and a strongly basic slag favor sulfur elimination from the bath. A high degree of oxidation of the bath hinders sulfur elimination because low manganese goes along with high FeO in the bath. As previously mentioned, the strongly reducing conditions in the presence of a basic slag, which one finds in the blast furnace, present a more favorable situation for sulfur elimination than one finds in the basic open hearth.

When other variables are maintained constant, increased temperatures favor sulfur elimination, the retention of manganese and phosphorus, and higher residual carbon concentrations.

The Finishing Period.—As is evident from the discussion of the refining period, a considerable concentration of FeO will be present in the bath after the metalloids have been eliminated. Therefore it is necessary either partly or fully to deoxidize the steel before it can be poured into molds. Furthermore, it usually is necessary to add certain alloying constituents or carburizers in order that the steel will meet the specifications set for the heat. These additions may be made in the furnace, in the ladle, or in the molds. For so-called quality steel, as much deoxidation as possible is done in the furnace so that the nonmetallic products of deoxidation (inclusions) may have a chance to rise out of the metal and join the slag before the heat is tapped. There is a limit, however, to the time a heat can be held in the furnace after the deoxidizer is added because iron oxides gradually diffuse into the metal from the slag, counteracting the effect of the addition, and a further carbon drop is obtained (heat "comes back on reboil"). There is, therefore, an economic balance, for any grade of steel, which governs the amount of deoxidation that should be practiced in the furnace and that which should be accomplished in the ladle. A small amount of deoxidation may be practiced by additions to the molds, but large additions to the steel in molds is prohibited unless the specifications on cleanliness (page 310) are very lax.

After making proper additions to the heat in the furnace and holding for a suitable time, the heat is tapped into a ladle; after making predetermined ladle additions, the heat is taken to the pour-

ing platform where it is "teemed" into ingot molds. Since the deoxidation and ingot-making stages in the manufacture of steel are very similar in all processes, these will be discussed in a later section. The entire time required for making a 100-ton heat of open-hearth steel is about 11 hr.

Products of the Basic Open-hearth Process.—Almost any grade of plain carbon or low-alloy steel may be made by the basic open-hearth process. The most important classes are: *structural steels* used in the fabrication of buildings, bridges, ships, cars, and other structures, mainly the low-carbon steels but including many varieties of alloy-treated steels; *copper-bearing steels* to resist atmospheric corrosion; plain carbon *spring steel; boiler* and *flange steel;* usually low- or medium-carbon grades which can be bent cold at sharp angles without cracking; *rail steel,* usually containing 0.60 to 0.85 per cent of carbon and suitable for railway rails; *pipe, skelp,* or *welding steel* of very low-carbon content; *sheet bar, tin bar,* and *sheet steel* of low-carbon content and suitable for rolling into sheets; *case-hardening steel,* the low-carbon plain or alloy steels which can be carburized (page 338) or casehardened; *strip steel, hoop iron, screw stock, forging steels,* and commercially pure irons, such as *ingot iron* and *Armco iron,* also made in large quantities in the basic open hearth.

The Acid Open-hearth Process

The acid open-hearth furnace is very similar in design and operation to the basic open hearth except that the hearth is lined with silica sand, an acid-type refractory (page 116). The acid hearth prohibits the use of basic slags and therefore limits the process to the production of steel from scrap and pig iron low in phosphorus and sulfur. Only 1.5 to 2.0 per cent of the steel made in the United States is made in the acid open hearth.

A typical acid open-hearth slag in per cent will run: FeO, 15; MnO, 21; SiO_2, 53; CaO, 4; and small amounts of Al_2O_3, etc. Owing to the combination of FeO with SiO_2, such a slag will be less oxidizing than a basic open-hearth slag of equal iron oxide content. As a consequence the bath is less oxidized at the end of the heat than in the basic process, less deoxidizer is required, and the amount of nonmetallic deoxidation product is less. For this reason, it is claimed that cleaner steel (fewer inclusions) can be produced by the acid than by the basic open-hearth process. Almost all acid open-

hearth steel is killed steel (page 303) and the bulk of it is used for forgings and steel castings.

Steelmaking in Electric Furnaces

Heat generated by the use of electric current was first used for melting steel by William Siemens in 1878. His steel-melting furnace consisted of a crucible with two horizontal carbon electrodes inserted through the wall of the crucible above the charge, which was heated by radiation from the arc between the electrodes (indirect arc furnace).

The next quarter-century was devoted principally to the development of new and more satisfactory types of electric furnaces and to their application in the production of ferroalloys (page 304). The first electric furnace for steel melting was installed in the United States in 1904. Since that time there has been a rapid increase in the use of electric furnaces for melting and refining high quality carbon and alloy steels. Table 54 fails to indicate the true importance of electric-furnace steels because they are worth from five to twenty times as much as the ordinary steels made by the bessemer and open-hearth processes.

Although many types of electric furnaces have been developed,[1] most of those used in America today are furnaces of either the Heroult direct-arc type or the coreless (high-frequency) induction type. The principal features of the direct-arc type of furnace are shown in Fig. 58. As indicated, the furnace may be provided with either a basic or an acid lining. Electrodes of carbon or graphite are suspended through the roof, which in many furnaces may be removed for charging the furnace. Current enters through one electrode, arcs to the metallic charge, travels through the solid or liquid charge, and arcs back to the other electrode. Furnaces of this type are built with capacities ranging all the way from 1 to 100 tons. Furnaces with capacities up to 60 tons have three electrodes on one three-phase circuit, but the larger furnaces have six electrodes on two three-phase circuits. Modern direct-arc furnaces are equipped with multivoltage transformers which permit the use of voltages ranging from 85 to 290 volts, and with devices that automatically regulate the positions of the electrodes.

[1] For a more detailed account of the development, design, and use of electric furnaces for steelmaking, see Camp and Francis, 5th ed., pp. 457–511; "Metals Handbook," 1939 ed., pp. 788–799.

The electric-furnace process offers certain advantages over other methods for steelmaking: (1) Heat may be supplied to the charge quickly and unusually high temperatures are attainable. (2) Temperatures may be regulated easily and maintained for any desired period of time. (3) There is no contamination of the charge from fuel or combustion products. (4) The molten charge may be treated under oxidizing, reducing, or neutral slags, and one slag may be removed and another produced without any difficulty. (5) Conditions can be controlled to eliminate or to prevent the elimination of constituents of the metal bath. Many alloying con-

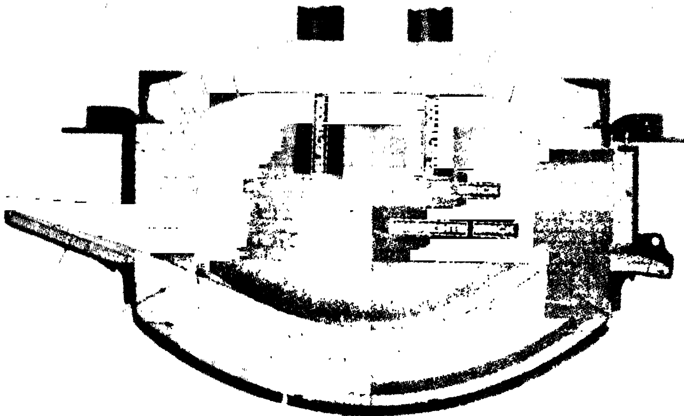


FIG. 58.—Direct-arc type electric furnace. (*From "Modern Refractory Practice, The Harbison-Walker Refractories Co.*)

stituents may be introduced into the bath by the reduction of their oxides in the slag. (6) The bath may be held at temperature for the elimination of nonmetallic inclusions before tapping. It is easier to produce clean steel by the electric process than by any other.

In general, electric furnaces are not used for making steel from pig iron. Electric steel is made (1) by melting, refining, and adjusting the composition of steel scrap or (2) by refining and adjusting the composition of basic open-hearth steel which has been transferred in a molten condition to the electric furnace.

The Basic Electric Process.—The basic-lined furnace of the Heroult type is especially adapted to the production of best quality carbon and alloy steels of the following varieties:

1. Stainless steels, containing 11 to 14 per cent of chromium.

2. Corrosion- and heat-resisting steels, containing 17 to 26 per cent of chromium and 8 to 13 per cent of nickel; also for steels of this grade containing 26 to 30 per cent of chromium and possibly small percentages of titanium, vanadium, selenium, columbium, or silicon.

3. Alloy and carbon tool steels.

4. High-speed tool steels.

5. Manganese steel (Hadfield steels), containing 12 to 15 per cent of manganese.

6. Magnet steels.

7. Alloy steels for special machinery parts.

If steel is made from a cold charge, scrap of suitable physical and chemical character is charged into the furnace and melted as rapidly as possible. After the charge is melted, burned lime, with some fluospar or sand to act as flux, is added to form a slag. Owing to the iron oxides on the scrap and formed during melting, this slag will be highly oxidizing as well as strongly basic. If phosphorus, carbon, manganese, etc., or a combination of these elements is to be eliminated, further additions of ore or mill scale may be made. If phosphorus, manganese, or chromium is to be removed, the black oxidizing slag containing these elements is removed ("pulled") at the proper time and a new white slag, which is basic but reducing in character, is made by additions of lime, small amounts of sand or fluospar, and coke dust. If the first slag was not pulled (not necessary to remove phosphorus, etc.), it may be changed over from a black oxidizing slag to a white reducing slag by the addition of various low-ash carbonaceous materials, which may be followed by ferrosilicon additions. These reducing slags contain some calcium carbide, formed by the action of carbon on CaO in the region of the arc. They may also be produced by direct additions of calcium carbide.

During the refining period under the reducing slag, a number of desirable reactions are accomplished:

1. Sulfur, present principally as FeS dissolved in the metal bath, may be quite completely eliminated as CaS in the slag. As has been previously mentioned, the presence of manganese increases the speed of sulfur elimination.

2. There is a considerable deoxidation of the bath due to diffusion of FeO to the slag where it is reduced by calcium carbide.

3. Alloying constituents may be added as ferroalloys without much loss due to the comparatively low degree of oxidation of the bath. Because of the reducing conditions, a number of alloying constituents may be introduced by adding their oxides to the slag where they are reduced, the free element then entering the metal bath. After the bath is brought to the proper alloy composition and is properly deoxidized, the slag is removed, the bath is recarburized if necessary, and the temperature is adjusted. The heat is then held for the proper time to eliminate nonmetallic inclusions and is tapped into the teeming ladle.

If basic electric steel is made by duplexing molten steel from the basic open hearth, refining is usually begun at the reducing slag stage in the electric furnace. The time required per heat in this practice is much less than in the "cold melt" process which has just been described.

The basic electric process has almost completely replaced the crucible process for making fine quality and special alloy steels.

The Acid Electric Process.—Heroult-type acid-lined furnaces are used principally in making steel castings and rarely for the production of ingots. As in all acid-type processes for steelmaking, phosphorus and sulfur cannot be eliminated in the acid electric process, and the raw materials for the charge must be selected to keep these elements low enough in the finished steel. The acid electric process is very similar to the acid open-hearth except that the electric process permits better control over all reactions and the production of "cleaner" steel.

Steelmaking in the Coreless Induction Furnace.—This furnace, often called the high-frequency induction furnace, is illustrated in Fig. 59. It consists of an acid- or basic-type refractory crucible or pot, *P*, surrounded by a water-cooled coil of flattened copper tubing, *C*, which serves as the primary for high-frequency current. Frequencies for the primary current may range from 500 to 60,000 cycles but the most common frequency is about 1,000 cycles. Inside the copper coil is placed a special refractory, *L*, and the space between this and the crucible is packed with a granular refractory, *R*. The bottom rests on fire-clay brick that is supported by the outer shell, *A*, of the furnace which is usually made of asbestos lumber or other strong nonmagnetic substance. As indicated, the entire furnace may be tilted for pouring. When a metallic charge is placed in the crucible and the high-frequency primary current is

applied, a heavy secondary current is induced in the charge which is dissipated as heat. After the charge is melted, the high motor effect of the current causes constant stirring and makes the bath very homogeneous.

From the time of its invention in 1917 until about 1924, the coreless induction furnace found use only in the laboratory. The first large furnaces were built in 1925 for melting nonferrous alloys; in 1926, the first commercial unit of 500-lb. capacity was installed for melting steel in England. Since 1929 the use of the furnace for the production of special steels and nonferrous alloys has expanded very rapidly in the United States, and recently installed furnaces have capacities as high as 5 tons. In some of the recent furnaces, the crucible has been designed to permit melting under vacuum so that oxygen, nitrogen, and hydrogen may be largely removed from a melt without the addition of "deoxidizers," etc.

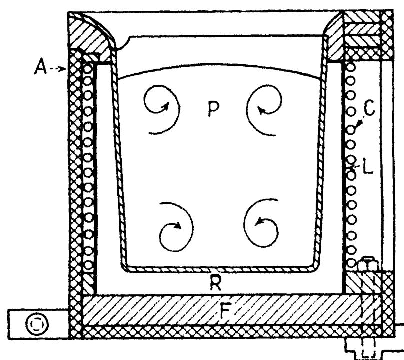


FIG. 59.—The coreless induction furnace.

Although it is possible to practice some refining by slags in the induction furnace, it is used principally for melting a charge of carefully selected materials without much change in composition. Steelmaking in the induction furnace is therefore almost identical with the older crucible process. The following materials are successfully made in the induction furnace:

1. High-quality, complex-alloy tool steels.
2. Extremely low-carbon alloys, such as magnetic alloys and stainless irons.
3. High-grade die steel, heat-resisting steel, etc., made by remelting the rolling-mill scrap of these same steels originally made in the arc furnace.
4. Hard carbides, such as the carbides of tungsten, chromium, and cobalt.

THE DUPLEX PROCESSES

The term duplex process may be applied to any combination of two steelmaking processes. In this country the unmodified term, duplex process, always refers to the combination of the acid

bessemer and the basic open-hearth processes. If the term is applied to other combinations of processes, it should be so indicated in the name; thus, a combination of the basic open-hearth with the basic electric process should be called the "duplex basic open-hearth—basic electric process." The latter practice already has been mentioned in the discussion of the basic electric process.

Acid Bessemer—Basic Open Hearth.—As usually carried out, this process consists of blowing basic iron in an acid-lined bessemer converter until the silicon, manganese, and a part of the carbon have been oxidized. The molten metal is then transferred to a large tilting basic open-hearth furnace where, in the presence of a basic oxidizing slag, the phosphorus and the remainder of the carbon are removed. In the finishing period, deoxidation, recarburizing, and teeming are practiced as in the regular open-hearth process. Only a portion of the metal bath is removed at any one time, fresh bessemer blown metal being added to a pool of already purified metal in the open hearth.

This process is especially suitable for making steel from the iron produced in the Birmingham, Ala., region. Iron in this district contains 0.80 to 0.85 per cent of phosphorus and therefore is intermediate between basic bessemer iron and the usual basic open-hearth iron. In the Birmingham practice, 8 to 10 tons of slag are made per heat and the slag, which contains 14 to 20 per cent of P_2O_5, is used as a phosphate fertilizer. The practice of eliminating most of the metalloids in the bessemer blow cuts the time per heat in the open hearth to from 4 to 6 hr., thus approximately doubling the capacity of the open-hearth furnaces. Since it operates on an all-hot metal charge, it is an especially attractive process in times when steel scrap is scarce and high in price.

Deoxidizing and Alloying Additions

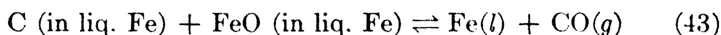
To bring about the elimination of carbon, silicon, etc., in steelmaking, it is necessary to provide a strongly oxidizing environment for the metallic charge. As a result, a heat of steel enters the finishing period in an oxidized state. Oxygen is present in liquid iron as FeO which will dissolve in liquid iron to the extent of about 0.95 per cent at 1520°C. (2768°F.) and 1.40 per cent at 1600°C. (2912°F.) when the iron is saturated with a pure iron oxide slag. When iron solidifies, there is an abrupt drop in the solubility of FeO to about 0.45 per cent in γ iron (page 313) and another drop to about 0.20 per cent in α iron. Steelmaking slags contain SiO_2,

CaO, etc., in addition to iron oxides, and as a consequence the per cent of FeO in liquid iron in equilibrium with a steelmaking slag will be less than the value given above.

FeO in the Steel Bath.—The equilibrium distribution coefficient for FeO between basic slags and metal at 1600°C. is

$$L = \frac{\%\text{FeO in slag}}{\%\text{FeO in metal}} = 60 \text{ to } 75 \qquad (42)$$

Another equilibrium, which is very important in determining the degree of oxidation of the metal bath, is



$$\text{C (in liq. Fe)} + \text{FeO (in liq. Fe)} \rightleftharpoons \text{Fe}(l) + \text{CO}(g) \qquad (43)$$

Since the concentration of liquid iron remains essentially constant and carbon monoxide is liberated at about atmospheric pressure, this equilibrium may be characterized by the fact that at any temperature the product of the carbon concentration and the FeO concentration in the liquid iron must be equal to a constant. In the region of steelmaking temperatures (1500 to 1600°C.), this product has the value

$$K = \%\text{C (in liq. Fe)} \times \%\text{FeO (in liq. Fe)} \cong 0.005 \text{ to } 0.012 \qquad (44)$$

As long as a carbon drop is taking place, FeO in the metal is not in equilibrium with either the FeO in the slag or the carbon in the bath. In a standard steelmaking practice, however, the operator may use either the degree of oxidation of the slag or the percentage of carbon in the metal to estimate the percentage of FeO in the bath. It is evident that with high-carbon heats the per cent of FeO in the bath will be low, but with low-carbon heats, the bath will be highly oxidized. To obtain proper behavior of the steel in the molds and to produce ingots of the desired properties, it is in general necessary to eliminate some or all of the FeO from the liquid steel.

Deoxidation.—The removal of FeO from liquid steel is referred to as deoxidation and is accomplished by the addition of some element to the steel, in the furnace, in the ladle, or in the molds, which forms an oxide more stable than FeO. Furthermore, the deoxidation product must be practically insoluble in the steel. The elements commonly used, arranged in the approximate order of their deoxidizing power, are Mn, Cr, Si, Ti, Mg, Ca, Zr, V, and Al.[1] Mn, Si and Al, singly, together, or in sequence, are extensively used as deoxidizers. The Mn and Si are invariably added in the form of

[1] Chipman, *Trans. A.S.M.*, **22**, 385 (1934).

standard grades of ferroalloys; Al is usually added in the form of shot.

Aluminum is the most powerful of the common deoxidizers. In making killed steels (page 307) it is usually added to the ladle after partial deoxidation in the furnace or ladle with other deoxidizers. Proper additions of aluminum not only complete the deoxidation, but may be used to control the grain size (page 332) of the steel. The relation between the percentage of FeO and that of residual Al in steel at three temperatures is shown in the deoxidation diagram (Fig. 60).

In addition to knowing the extent to which a certain element will deoxidize steel, the metallurgist is interested in knowing the

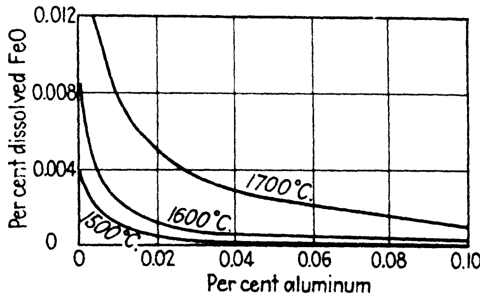


Fig. 60.—Relation between residual aluminum and FeO in steel.

properties of the products of the deoxidation. Since these in general possess very little solubility in the liquid steel, they will appear in the finished product as inclusions unless they are given an opportunity to escape before the solidification of the steel in the molds. A liquid deoxidation product, or one that will flux with FeO or MnO to form a liquid product, will coalesce to form larger particles and more rapidly rise out of the steel bath than a solid finely divided deoxidation product. In making clean steel, it is a common practice to deoxidize partly with ferromanganese and ferrosilicon, or silicomanganese in the furnace, where, due to the comparatively shallow bath and liquid deoxidation products, the inclusions have an opportunity to rise to the surface before the heat is tapped into the ladle.

In making rimming and semikilled steels, aluminum is added in the molds to diminish the active FeO content and to control the action in the molds.

Alloying Additions.—As will be noted from the above list of deoxidizing agents, most of the common alloying agents with the

exception of copper and nickel will deoxidize liquid steel. For this reason, no appreciable residual concentration of alloying element can be present in a steel unless it is quite completely deoxidized and the alloy steels as a class are killed steels. The more common grades of materials used for deoxidation and for alloying additions are listed in Table 56.

TABLE 56.—TYPICAL COMPOSITIONS OF FERROALLOYS, PER CENT (IRON CONTENT OMITTED)*

Material	C	Mn	P	S	Si	Cr	V	Mo
Spiegel	5.50	19.00	0.04	.....	1.75			
Ferromanganese	5.21	78.90						
Ferromanganese	1.22	83.0	1.56	0.015	1.37			
Ferromanganese	0.05	83.0						
50% Ferrosilicon	0.06	0.30	0.024	0.015	48.24			
75% Ferrosilicon	0.02	0.23	0.021	0.014	76.68			
10% Ferrosilicon	1.13	0.28	0.146	0.040	10.12			
Silicospiegel	4.07	18.90	......	.....	3.51			
Silicospiegel	3.46	31.20	......	.....	7.86			
Silicomanganese	2.40	68.75	0.039	0.056	15.69			
Ferrophosphorus	0.11	1.90	24.20	.....	1.16			
Ferrochrome	5.34	....	......	.....	1.45	70.1		
Ferrochrome	0.06	....	......	.....	1.00	70.0		
Ferrovanadium	1.00	0.36	......	.....	4.00	....	38.0	
Ferromolybdenum	1.00	....	......	.....	1.00	....	....	60.0

* For a more detailed discussion of the available grades of ferroalloys see "Metals Handbook,' 1939 ed., pp. 803–808. Copper, nickel, and aluminum are used in the form of comparatively pure metals.

THE PRODUCTION OF STEEL INGOTS

Steel produced by any of the processes leaves the steel plant in the form of castings called ingots, made by tapping the heat from the furnace into a ladle and then teeming the molten steel into ingot molds of suitable size and shape. Although *lip-pour ladles* are used to some extent in steel foundries and bessemer plants, the greater portion of steel is teemed from *bottom-pour ladles* designed as illustrated in Fig. 61. It is the aim in ingot making to produce a casting as homogeneous as possible in both its chemical and physical properties. In making a heat of steel, furnace practice, means and extent of deoxidation, recarburizing practice, tapping temperature, teeming temperature, etc., all have an important bearing upon the quality of the final ingot. Other factors such as rate of teeming, mold design, mold treatment and temperature, additions to the steel in the molds, etc., exercise an equally important influence on ingot

quality. It certainly is true that incorrect teeming practice may yield defective ingots even when the best practice has been followed in making the steel.

After the ingot is partly or wholly solidified, the mold is removed by the *stripper crane* and the ingot transferred to a *soaking pit*,[1] where it is brought to a uniform temperature throughout, suitable for hot working in the blooming mill, slab mill, forging press, etc.

From the standpoint of the behavior of the steel during solidification, steel ingots may be classified as *killed*, *semikilled*, *rimmed*, or *capped*.

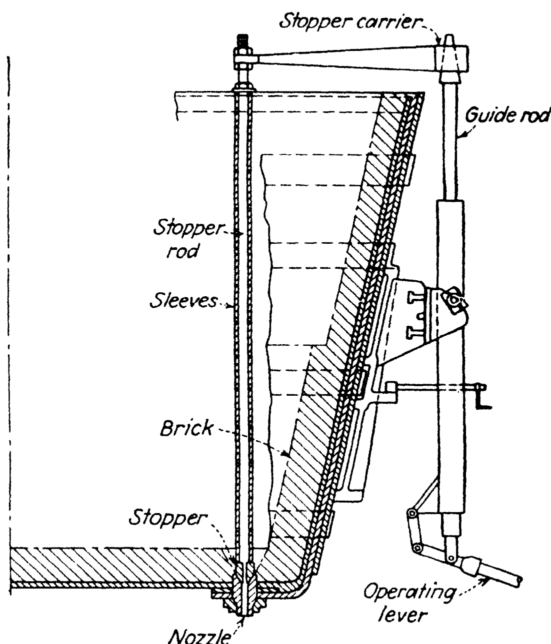


Fig. 61.—Cross section through a bottom-pour teeming ladle.

Ingot Molds.—The small molds, 3 to 6 in. square, used for many of the special steels, are often of the split or two-piece variety to facilitate removal. The bulk of steel produced, however, is teemed into single-piece cast-iron molds. These large molds fall into two classes: big-end-up and big-end-down, as illustrated in Fig. 62. Big-end-down molds are open at both ends and are set on a cast-iron or copper stool which forms the bottom of the mold. These molds have the advantages of lower first cost and easier stripping from the ingot. Big-end-up molds usually have a round tapered hole in

[1] Camp and Francis, 5th ed., pp. 659–667.

the bottom which is closed with a plug. Many modifications of these two main classes of molds are in use: in cross section they may be square, rectangular, round, corrugated round, fluted, etc. In general, sharp corners should be avoided in mold design. Big-end-up molds usually are equipped with refractory "hot tops" or "sinkheads" (Fig. 62) to keep a reservoir of molten metal to feed the upper central portion of the ingot during solidification and thus prevent the formation of a pipe cavity in the ingot proper. A modification of the big-end-down mold is the bottleneck mold in which the top is built to permit the placing of a heavy metal cap on the liquid steel, causing rapid cooling and quick solidification of the top portion of the ingot. Before use, molds are carefully

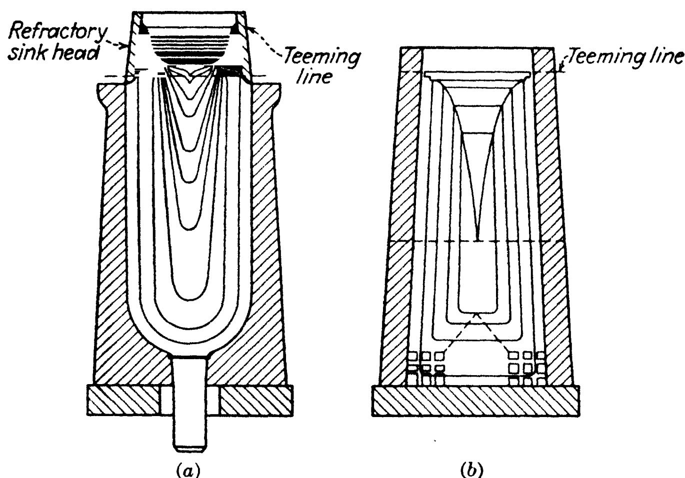


Fig. 62.—(a) Big-end-up, and (b) Big-end-down ingot molds.

cleaned, inspected for surface defects, and then sometimes coated with whitewash, tar, or finely divided carbon from a smoky flame. In some plants, molds are coated by dipping in a brine solution. Molds should be dry and warm when steel is teemed into them.

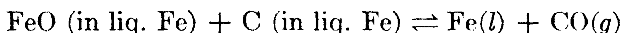
Most steel is teemed into molds by bringing the nozzle of the bottom-pour ladle containing the steel over the center of the top of the mold. The rate of rise of the steel in the mold is important and may be regulated to the rate best suited for a given grade of steel and mold size by selecting the nozzle size. Steel should be teemed with the nozzle full open to prevent splashing on the mold walls. In some plants, certain grades of killed steel are bottom poured; the steel is teemed into a refractory-lined funnel from which it is led in closed runners to the bottom of the mold.

Crystallization of Steel, and Ingot Defects.—As soon as molten steel is poured into a mold, the metal begins to crystallize on the walls and the bottom, producing what is called the *skin* of the ingot. This skin continues to grow as heat is lost by the metal. As the mold temperature and the skin thickness increase, the rate of heat loss and hence the rate of solidification decrease. In big-end-down ingots the skin, due to the contraction accompanying solidification, finally draws away from the mold wall leaving an insulating air gap which further decreases the rate of heat loss. An ingot 18½ by 20 in. will require 65 to 80 min. for complete solidification. A slow rate of crystallization may lead to the growth of very large dentritic (page 216) or columnar crystals which extend from the outer skin toward the center of the ingot. This condition is sometimes called *ingotism* and may cause planes of weakness extending from the corners and edges of the ingot. *Ingot cracks* may open along these planes in the subsequent hot-working operations.

After a rigid skin is formed on the ingot, the shrinkage space due to further solidification is fed by the liquid metal still remaining in the upper central portion. As a consequence, after complete solidification, a cone-shaped shrinkage cavity called a *pipe* is left in the upper part of the ingot. If no *blowholes* are formed during solidification, as is the case with thoroughly deoxidized or "killed" steel, the pipe cavity will equal 2 to 4 per cent of the ingot volume and may extend two-thirds of the way to the bottom of the ingot. For this reason killed steels are almost always teemed into big-end-up molds equipped with hot tops (see Fig. 62). The hot top provides a supply of molten steel which feeds the ingot proper during solidification and brings the pipe into the small upper portion of the ingot. The surface of a pipe cavity becomes oxidized and, since such surfaces will not weld together in hot working, the pipe will appear in the smallest rod or wire made from that portion of the ingot. The portion of an ingot containing the pipe cavity therefore must be cropped and returned as scrap. For this reason, the steelmaker uses every means at his command to reduce the amount of pipe and to cause it to form in the extreme upper part of the ingot. The method for eliminating pipe from the ingot proper in making killed steels already has been described. Most high-carbon and alloy steels are killed steels; they are normally partly deoxidized in the furnace with ferromanganese followed by ferrosilicon or by silicomanganese and held to permit at least partial elimination of the deoxidation products (inclusions). Deoxidation is then completed

by additions of aluminum or other strong deoxidizers to the steel in the ladle. To make clean steel (low in inclusions), as much deoxidation as possible should be accomplished in the furnace.

Rimming or effervescing steels represent the other extreme from killed steels. They usually are steels containing 0.05 to 0.15 per cent of carbon (it is practically impossible to get rimming action in steels containing over 0.25 per cent of carbon) and as a consequence they contain a high FeO content when tapped. When these steels are teemed into molds, crystallization to form the skin results in an increase in the FeO and C concentration to above the equilibrium concentrations in the liquid steel. These substances therefore react and the CO gas evolved causes vigorous convection in the liquid steel.



$$\text{FeO (in liq. Fe)} + \text{C (in liq. Fe)} \rightleftharpoons \text{Fe}(l) + \text{CO}(g)$$

Other gases, especially nitrogen and hydrogen, are thrown out of solution as the steel solidifies and are evolved with the carbon monoxide. This phenomenon, known as *rimming*, produces beneficial results: it washes the surface of the growing skin and thus prevents the entrapment of mother liquor in growing crystals. This serves to produce a tough sound skin of almost pure iron, essentially free from blowholes and inclusions. The rimming action also keeps the top of the ingot open until a skin of sufficient thickness has formed. Once the skin has formed, a steel plate usually is placed over the portion of the top remaining open to cause rapid solidification of the top while the central portion still is liquid. The evolution of gas continues in the center, but instead of escaping it now forms *blowholes* which occupy sufficient volume so that no pipe is formed. These blowholes are deep seated (considerable distances from the surface of the ingot), their surfaces are not oxidized, and they therefore are welded together as the gas leaves the ingot by diffusion during hot working. The bulk of low-carbon steel sheets, used for automobile fenders and bodies and other products requiring a good surface, are made from rimmed ingots. In making rimmed steel only enough deoxidation (usually in the ladle) is practiced to control the FeO to give proper rimming action in the molds. Often the addition of small amounts of aluminum to the molds may assist in obtaining the proper rimming action, probably because the refractory Al_2O_3 particles formed in the reaction



$$2\text{Al} + 3\text{FeO} = 3\text{Fe} + \text{Al}_2\text{O}_3$$

serve as points upon which bubbles of CO may more readily be formed.

In between killed steels and rimmed steels are the *semikilled* and *capped* steels. Many of the common structural and trade steels ranging in carbon from 0.10 to 0.30 per cent are made as semikilled steels. In making these steels, sufficient deoxidation (mostly in the ladle) is practiced to give an ingot free of blowholes near the surface and still obtain enough action in the molds to prevent the formation of extensive pipe. Capped steels are teemed in bottleneck molds, are sufficiently deoxidized to prevent appreciable rimming action, but with sufficient action to make the steel rise into the bottleneck where it solidifies when it comes in contact with the heavy steel cap. The remainder of the steel solidifies with the formation of deep-seated blowholes but very little pipe.

Although deep-seated blowholes weld up during hot working, blowholes near the surface must be considered an ingot defect. During hot working or scaling these blowholes may be exposed, leading to oxidation of the surface of the cavity. Once oxidized, they do not weld together and lead to seams and other surface defects in the finished product.

In addition to the ingot defects already discussed (ingotism, pipe, blowholes, seams), internal cracks or "flakes," scabs, segregation, and inclusions deserve some attention. Internal cracks may result from stresses produced during solidification or during reheating, especially if the rate of heating is too great. They also may develop along planes of weakness where columnar crystals meet if the initial hot work is too severe. Scabs on the ingot surface usually result from particles of slag which adhere to the mold walls as the steel rises in the mold during teeming. They may also result from liquid metal breaking through the ingot skin after it has begun to form. Since these surface defects will appear in the finished product, they must be removed from the ingot, usually by chipping, before hot work is begun.

All the constituents present in the finished ingot, except particles of slag and of deoxidation products, are homogeneously dissolved in the liquid steel. As iron solidifies, these constituents will distribute themselves between the solid phase and the remaining mother liquor in a manner dependent upon their relative solubilities in liquid and solid iron. Those substances which have much higher solubility in liquid than in solid iron will tend to accumulate in the mother liquor and hence will be present at higher concentrations

in the last steel to solidify. This variation in concentration of a constituent throughout an ingot is called segregation. There is not much difference between the concentrations of Si, Mn, Ni, Cr, and V in the liquid and solid phases; as a consequence, there is no appreciable segregation of these elements in an ingot. Carbon and phosphorus show considerable segregation, these elements usually being present in the upper central portion of the ingot at higher concentrations than in the sides and bottom. There is still greater segregation of such constituents as FeO, FeS, MnO, and MnS, because these substances are only very slightly soluble in solid iron. Segregation is not so great as one might expect on a basis of the relative solubilities of the constituents in liquid and solid iron. Actually much of the mother liquor is entrapped by growing crystals throughout the ingot and this leads to a more uniform distribution of all elements in the steel.

Particles of nonmetallic matter present in the solidified ingot, but not dissolved in the solid steel, are called inclusions. Depending upon their size, composition, and distribution, they may adversely affect the physical properties of a steel. A "clean" steel is one of low-inclusion content, and a certain cleanliness, as rated by microscopic examination, is written into the specifications for many grades of steel. Inclusions frequently are divided into the following classes:

1. Accidental inclusions; which usually are large in size and consist of particles of slag carried over from the furnace, small bits of refractory from the furnace runner or the ladle lining, etc. With reasonable care, inclusions from this source may largely be eliminated.

2. Inclusions consisting of products of the deoxidation of steel. These usually are substances such as alumina, silica, iron silicate, manganese silicate, and aluminum silicate. If steel is to be freed of these substances, it must be held after deoxidation for a sufficient time to allow these deoxidation products to rise to the surface. It is the consensus of opinion that the products formed in furnace deoxidation can to a considerable extent be eliminated; the products of ladle deoxidation are only partly eliminated and those formed by deoxidation in the mold almost certainly remain in the solidified ingot.

3. Inclusions composed of substances that were soluble in liquid steel but precipitated due to decreased solubility as the liquid cooled

and solidified. In this class one finds principally FeO, FeS, MnO MnS, etc.

Inclusions should not invariably be considered an unmitigated evil. For example, finely divided Al_2O_3 is used to control grain size in the production of "*fine-grained*" steels; sulfide inclusions contribute an ease of machinability highly desirable in screw stock.

The whole problem of proper ingot practice, the phenomena connected with the solidification of steel,[1] and the influence of inclusions on physical properties have engaged the attention of many investigators in recent years with the result that steel quality has been enormously improved.

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[1] Hayes and Chipman, *Trans. A.I.M.E.*, **135**, 85 (1939). Hultgren and Phragmen, *ibid.*, **135**, 133 (1939). In these papers many references are given to the literature on the subject.

CHAPTER VII

ALLOYS OF IRON

CONSTITUTION, TREATMENT AND USES

By J. C. Warner, Ph.D.

Iron and its various alloys are probably our most important materials of construction. In a broad sense these materials may be classified into the following groups: wrought iron and open-hearth irons, plain carbon steels, alloy steels, special ferrous alloys, and cast irons. The production of these materials was described in Chap. VI but much remains to be said about the relationship between properties and composition, and about the way in which desirable properties may be developed by suitable treatments, such as normalizing, annealing, hardening, tempering, and case-hardening. The study of these subjects constitutes that branch of science and engineering which is known as ferrous metallography or the physical metallurgy of iron and steel. Any logical approach to this study requires that one, first of all, become thoroughly familiar with the physical properties of pure iron in its several allotropic modifications and with the iron-carbon constitutional diagram. The next section therefore deals with these subjects.

Iron and the Iron-carbon Constitutional Diagram

Relatively pure iron (commercially pure iron) may be made by the electrolytic refining of iron or steel scrap, by forming iron carbonyl from impure iron and then decomposing the iron carbonyl, or by the careful and drastic purification of pig iron and steel scrap in the basic open-hearth furnace. Electrolytic iron will contain about 0.10 per cent, carbonyl iron about 0.05 per cent, and open-hearth iron approximately 0.20 per cent of impurities.[1] Still purer iron has been prepared, but only on a laboratory scale; the above-mentioned irons are available in commercial quantities.

The Allotropy and Properties of Iron.—Pure iron at ordinary pressures and at temperatures up to 910°C. (1670°F.) exists as

[1] For a complete analysis of these irons see Camp and Francis, 5th ed., p. 826; "Metals Handbook," 1939 ed., p. 424.

an allotropic (page 162) modification known as alpha (α) iron. Between 910 and 1403°C. (2557°F.), the stable allotropic modification is gamma (γ) iron. At 1403°C., γ iron transforms into delta (δ) iron and δ iron melts at 1535°C. (2795°F.). Liquid iron boils at about 3000°C. (5430°F.). α iron atoms are arranged in a body-centered cubic space-lattice,[1] but the space arrangement of atoms in crystals of γ iron is face-centered cubic. δ iron also possesses a body-centered cubic lattice and appears to be identical with α iron as an allotropic modification. Thus, if one plots a property of iron,

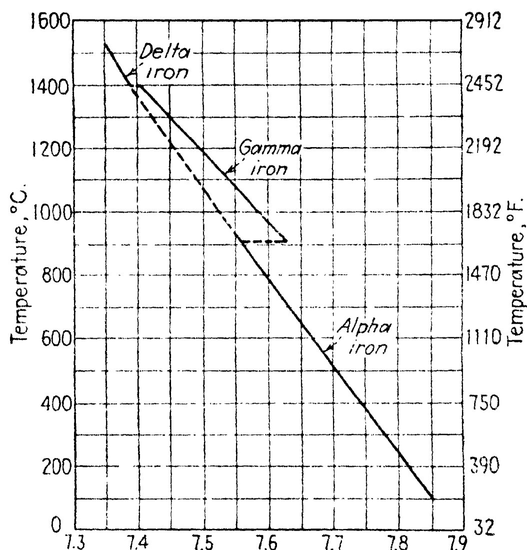


FIG. 63.—Density (grams per cubic centimeter) of iron as a function of temperature.

such as density, against temperature (Fig. 63), the curve for δ iron will clearly appear as an extension of the curve for α iron.

Many of the physical as well as the electrical and magnetic properties of iron are considerably altered by the presence of small amounts of certain impurities or by mechanical and heat-treatment of the iron. Pure iron is very easily magnetized when placed in a magnetic field; it promptly loses its magnetism when the field is removed. The presence of small amounts of impurities may greatly alter the field strength required to produce a certain degree of magnetization and magnetism produced in such irons may persist after the field is removed (hysteresis loop between the curves for magnetization and demagnetization[2]). When α iron is heated

[1] "Metals Handbook," 1939 ed., p. 424.

[2] "Metals Handbook," 1939 ed., p. 435.

it becomes less magnetic; the magnetization begins falling off rapidly in the range 750 to 768°C. and is lost almost completely at about 790°C., the Curie point. Thus, α iron is paramagnetic from 790°C. to the transition temperature, 910°C. Gamma iron and δ iron are paramagnetic. In the earlier literature, paramagnetic α iron was designated as β iron. There is, however, no justification for the designation because the loss in magnetization is gradual; it is not accompanied by a change in crystal structure, or by any of the other changes characteristic of a definite transformation from one allotropic modification to another. Pure iron and the various kinds of commercially pure iron are soft and ductile, and have a low tensile strength compared to steels. For example, an Armco ingot iron containing 0.015 per cent of C, 0.025 per cent of Mn, 0.003 per cent of Si, 0.005 per cent of P, and 0.025 per cent of S, when annealed will have approximately the following tensile properties (pages 125–130): 45,000 psi tensile strength; 30,000 psi yield strength; 35 to 40 per cent elongation in 2 in.; and 70 to 75 per cent reduction in area. For a complete discussion of the properties of iron the reader is referred to the larger treatises.[1]

The Iron-Iron Carbide Constitutional Diagram.—The equilibrium relationships in alloys of iron and carbon (iron and iron carbide), over the practical ranges of temperature and carbon concentration, are shown in Figure 64. Such phase diagrams have been discussed in Chap. V, page 206. Any point in the diagram represents a definite alloy at a definite temperature, the carbon content being shown on the horizontal axis directly below the point and the temperature on the vertical axis directly opposite the point. Whenever an alloy is heated or cooled so that a line on the diagram is crossed, a phase change occurs. All alloys represented by compositions and temperatures in the region above *ABCD* are completely liquid. When liquid alloys containing up to 4.3 per cent of carbon are cooled to temperatures on the curve *ABC*, solid crystals begin to form. *ABC* is called the "*liquidus*" for these alloys. If the alloy contains from 0 to 0.55 per cent of C, the first crystals formed will be a solid solution of carbon in δ iron. The first crystals formed from alloys containing 0.55 to 4.3 per cent of carbon are of austenite, a solid solution of carbon in γ iron. In the region between the liquidus and *AHJEC*, the liquid melt and

[1] CLEAVES and THOMPSON, "The Metal—Iron," McGraw-Hill Book Company, Inc., New York (1935). "Metals Handbook," 1939 ed., pp. 242–256. RALSTON, *U. S. Bur. Mines Bull.* 296.

solid crystals exist together in equilibrium (page 218). Whenever an alloy containing up to 4.3 per cent of carbon is cooled to *AHJEC*, it becomes completely solid and *AHJE* is called the "solidus" for alloys in this range of composition.

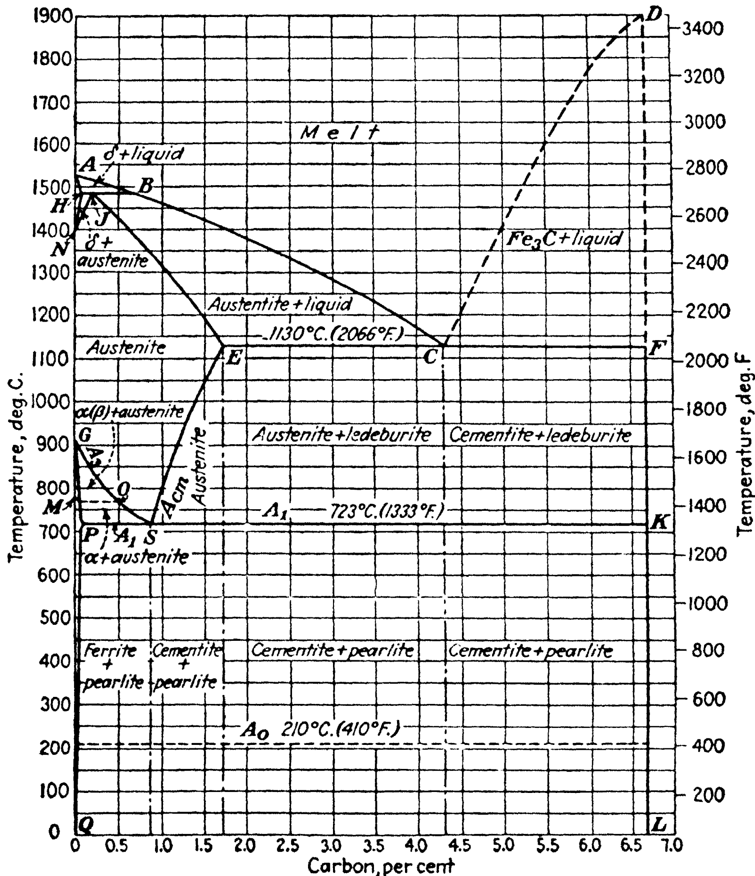


FIG. 64.—The iron-iron carbide constitutional or phase diagram (*From Epstein "Alloys of Iron and Carbon," Vol. I, McGraw-Hill Book Company, Inc.*)

When liquid alloys containing more than 4.3 per cent of carbon are cooled to temperatures on the curve *CD*, solid crystals of *cementite* (iron carbide, Fe_3C) begin to form; hence *CD* is called the liquidus for these alloys. When any alloy containing over 4.3 per cent of carbon has been cooled to *CF*, it becomes completely solid. The alloy containing 4.3 per cent of carbon is the *eutectic* (page 209) alloy, and it will therefore solidify completely at *C*,

1130°C. (2066°F.) with the simultaneous formation of austenite and cementite, the solid eutectic mixture.

The region of the diagram (Fig. 64) in which δ iron may exist, *ABJN*, is not very important in practice because temperatures between the melting point of iron and 1400°C. are not employed in the various mechanical working or heat-treating processes. Furthermore, rates of transformation and diffusion in this temperature range are so rapid that even a steel that has been rapidly cooled to slightly below 1400°C. will consist entirely of austenite

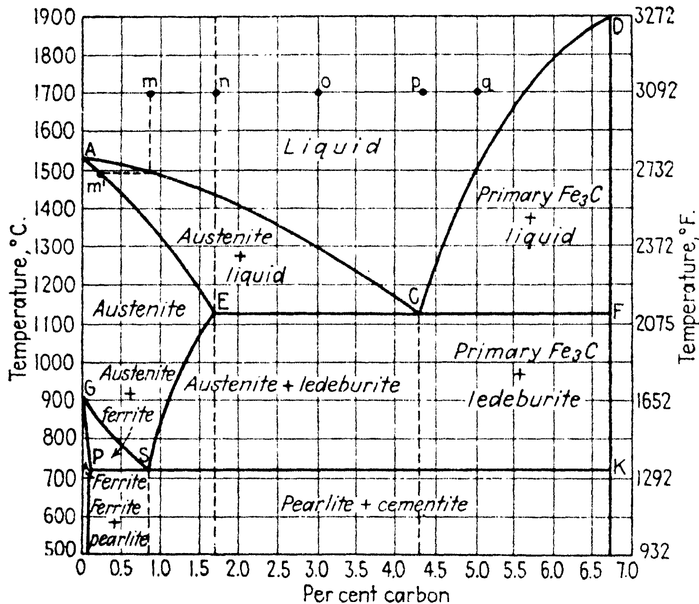


FIG. 65.—The iron-iron carbide diagram omitting the delta region.

crystals. It is possible, therefore, to discuss all the important practical aspects of the solidification and heat-treatment of steels and cast irons by the use of the somewhat simplified iron-iron carbide diagram which is given in Fig. 65. Iron-carbon alloys containing up to 1.7 per cent of carbon are classed as *steels* and those containing over 1.7 per cent of carbon are called *cast irons*. Actually, the alloys containing from about 1.7 to 2.0 per cent of carbon and those containing over 5.0 per cent of carbon are not of much practical importance.

Solidification of Iron-carbon Alloys.—Making use of Fig. 65, let us now consider the course of events when liquid alloys of various

carbon contents are cooled to a temperature just below the eutectic temperature, 1130°C. (2066°F.), represented by the line *EF*. If an alloy containing 0.80 per cent of carbon is cooled from point *m* on the diagram, it will remain liquid until cooled to the liquidus, *AC*; at this temperature crystals of austenite, of composition *m*,' given by drawing a horizontal to the solidus, will separate from the melt. Since these crystals are poorer in carbon than the melt, the percentage of carbon in the melt will increase as crystallization proceeds, the temperature and composition of the liquid following the liquidus *AC*. When the temperature has dropped to a value at which the percentage of carbon on the solidus curve *AE* is the same as for the original liquid alloy (0.8 per cent), the alloy will become completely solid and will consist entirely of crystals of austenite.

When a liquid alloy containing 1.7 per cent of carbon is cooled from point *n*, a process entirely analogous to the above will take place. Austenite crystals will begin to form when the curve *AC* is reached; as crystals separate, the liquid becomes richer in carbon and the last drop of liquid, containing 4.3 per cent of carbon, will solidify when the eutectic temperature (1130°C.) is reached. At this temperature, the completely solidified alloy will consist entirely of austenite crystals containing 1.7 per cent of carbon dissolved in solid solution in γ iron.

A liquid alloy containing 3.0 per cent of carbon (point *o* on diagram) when cooled will begin to form austenite crystals when *AC* is reached and as before the percentage of carbon in the melt will increase as solidification proceeds. In this case, however, considerable liquid containing 4.3 per cent of carbon will remain when the eutectic temperature is reached and this will solidify forming the eutectic conglomerate structure of alternate masses of austenite (saturated with carbon, 1.7 per cent of carbon) and cementite. This eutectic structure is easily recognized as characteristic by microscopic examination and one may readily distinguish eutectic austenite from the austenite that separated from the liquid melt before the eutectic temperature was reached. Austenite formed by crystallization from the melt above the eutectic temperature is called *primary austenite*.

If one cools an alloy of exactly the eutectic composition, 4.3 per cent of carbon, from a temperature corresponding to point *p*, the alloy will remain entirely liquid until the eutectic temperature (1130°C.) is reached. At this temperature, the alloy will solidify completely, forming the eutectic conglomerate of austenite and

cementite, no primary crystals being present in the solid mass. The name *ledeburite* has been applied to this eutectic of saturated austenite and cementite. At the eutectic, the liquid phase (melt) is in equilibrium with two solid phases (cementite and saturated austenite). With these three phases in equilibrium in the two component system, the system will have zero degrees of freedom (invariant) (page 207); liquid therefore must change to solid at constant temperature when heat is lost by the system.

Finally, consider a liquid alloy containing 5.0 per cent of carbon at a temperature indicated by the point *q*. On cooling, this alloy remains liquid until the liquidus *CD* is reached, whereupon crystals of *primary cementite*, Fe_3C, begin to form from the melt. Since cementite is richer in carbon (6.67 per cent of carbon) than the melt, the carbon content of the liquid decreases with drop in temperature along *DC*. When the eutectic temperature is reached the remaining liquid will have the eutectic composition (4.3 per cent of carbon) and will solidify at the eutectic temperature forming the solid eutectic of saturated austenite and cementite, ledeburite. This alloy when completely solidified therefore will consist of primary cementite and ledeburite, whereas the solidified 4.2 per cent alloy consists entirely of ledeburite. The solidified 3.0 per cent alloy was composed of primary austenite and ledeburite, and the 0.80 and 1.7 per cent alloys when cooled just below the solidus *AE* were made up entirely of austenite.

Iron-carbon alloys containing exactly 4.3 per cent of carbon are called *eutectic cast irons;* those containing over 4.3 per cent of carbon are named *hypereutectic* (*hyper*, over); those with between 1.7 and 4.3 per cent of carbon are known as *hypoeutectic* (*hypo*, less than) cast irons.

The characteristic microstructure of an alloy of the hypereutectic type is shown in the photomicrograph of Fig. 66.

Transformations in Solid Iron-carbon Alloys.—It already has been mentioned (page 313) that when pure γ iron is slowly cooled through 910°C. (1670°F.) it undergoes an allotropic transformation into α iron. γ iron in which carbon is dissolved to form austenite likewise transforms into α iron when cooled to the proper temperature. The temperature at which transformation begins, however, depends in this two-component system upon the carbon content of the austenite and is given by the curve *GS* in Figs. 64 and 65, for steels containing from 0 to 0.83 per cent of carbon. The curve *SE* (A_{cm} line) represents the solubility of cementite in austenite

at all temperatures from 723°C. (1333°F.) to 1130°C. (2060°F.). As has been mentioned, austenite saturated with cementite at 1130°C. contains 1.7 per cent of carbon. The solubility decreases with decrease in temperature, however, and austenite saturated with cementite at 723°C. contains only 0.83 per cent of carbon. In spite of the decreased solubility of cementite in γ iron at the lower temperatures, it is still much higher than the solubility of cementite in α iron, as is indicated by the curve *GPQ* on the diagram. When α iron is saturated with cementite, the per cent of carbon is about 0.04 at 723°C. and decreases to about 0.005 to

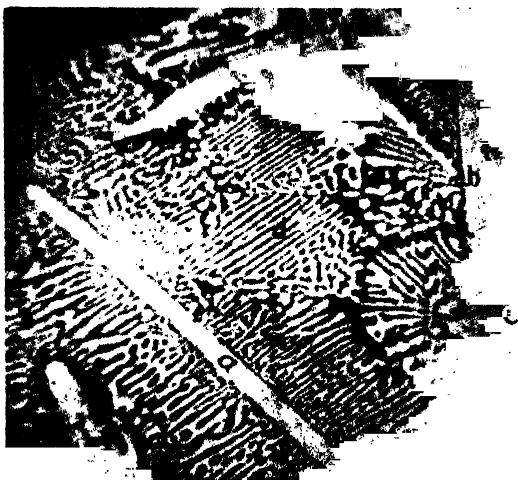


FIG. 66.—Hypereutectic cast iron. The white bands, *a*, *b*, and *c* are primary cementite; the striated mass *d* is the eutectic (ledeburite). Magnified 30 diameters. (*Howe.*)

0.008 per cent at room temperature. A solid solution of cementite or any other constituent of steels in α iron is called *ferrite*.

Because of the much greater solubility of cementite in γ iron than in α iron, the presence of carbon in austenite depresses the transformation below the temperature at which it occurs in pure γ iron. This portion of the iron–iron carbide diagram is shown on a larger scale in Fig. 67 because the transformations and equilibrium relations in this region are of fundamental importance in heat-treating, normalizing, quenching, and annealing. To understand this portion of the diagram, let us study the changes that will take place when steels of various compositions are *very slowly* cooled through the critical region, *i.e.*, from above *GSE* to below *PSK*.

If one cools a steel containing 0.30 per cent of carbon from 1000°C. (or any temperature above *GS*) where the steel is entirely austenitic, nothing will happen until a temperature of 800°C., on the line *GS*, is reached.

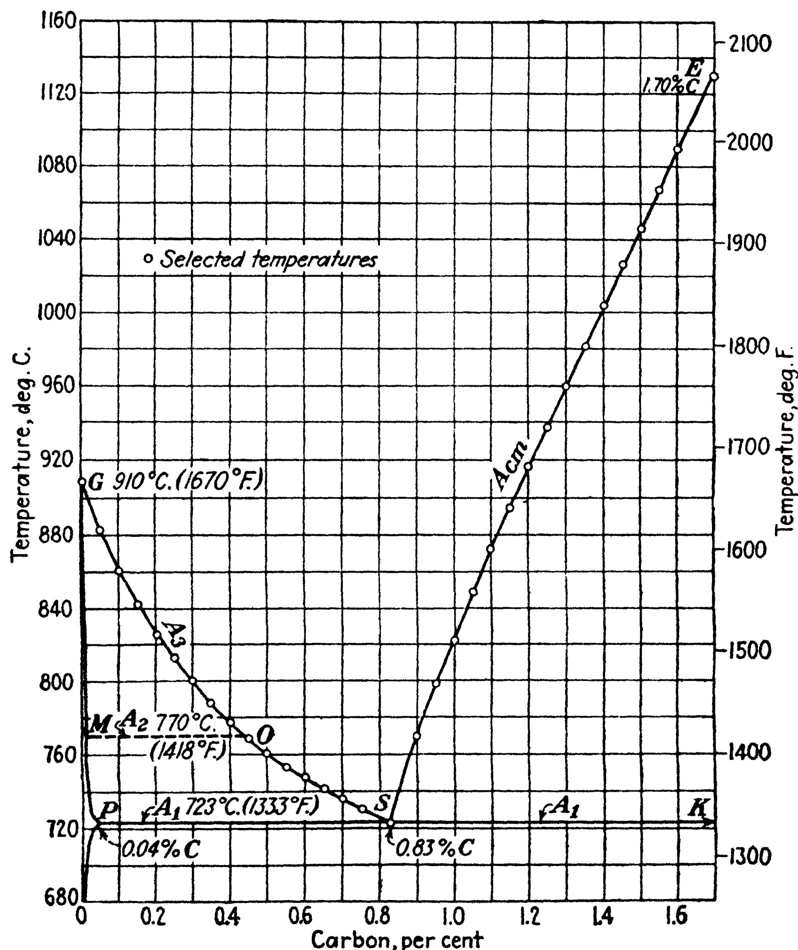


FIG. 67.—The eutectoid region of the iron-iron carbide diagram. (*From Epstein "Alloys of Iron and Carbon," Vol. I, McGraw-Hill Book Company, Inc.*)

At this temperature the γ iron in austenite will begin to transform into α iron; crystals of ferrite (α iron containing only a minute amount of dissolved carbon) will form and the "mother" austenite will increase in carbon content with further cooling along the line *GS*. When a temperature of 723°C. (1333°F.) is reached,

the remaining austenite will contain 0.83 per cent of carbon and will be saturated with respect to both ferrite and cementite. Further loss of heat by the system will cause the remaining austenite to transform completely into ferrite and cementite without change in temperature. At 723°C. with 0.83 per cent of carbon, a situation has been encountered which is very similar to the eutectic at 1130°C. with 4.3 per cent of carbon. Three phases, austenite, ferrite, and cementite, are in equilibrium in a two-component system leaving zero degrees of freedom. Hence, to change the temperature at least one phase must disappear. Because of its similarity to a eutectic, the point at 723°C. and 0.83 per cent of carbon is called a *eutectoid* (page 221).

The ferrite and cementite that form at the eutectoid occur as alternate thin lamellae which have very much the same appearance as many of the ordinary eutectic mixtures previously described. At low magnifications these eutectoid lamellae have a pearly appearance. For this reason, this metallographic constituent of steels long ago was given the name *pearlite*.

Ferrite rejected from the austenite before the eutectoid is reached is called proeutectoid ferrite; that which is a part of the pearlite is known as eutectoid ferrite. Incidentally, it should be mentioned that all ferrite at temperatures below *MO* is magnetic. Austenite is paramagnetic and cementite likewise is paramagnetic until it is cooled to below 210°C. (410°F.).

When a steel in the austenitic state containing exactly 0.83 per cent of carbon[1] is cooled, no change occurs until the eutectoid point, *S*, is reached. Further loss of heat will cause complete transformation of the eutectoid austenite into pearlite.

Consider, next, austenite containing 1.3 per cent of carbon. When this alloy is cooled to 960°C. (on the curve *SE*, called the A_{cm} line), crystals of cementite begin to form. Since cementite contains 6.68 per cent of carbon, its separation causes a progressive decrease in the carbon content of the austenite as the temperature drops. Finally at 723°C., the remaining austenite will contain exactly 0.83 per cent of carbon and will transform into pearlite at the eutectoid temperature. The cementite that separates from

[1] MEHL and WELLS, *Trans. A.I.M.E.*, **125**, 429 (1937), find 0.80 per cent of carbon as the eutectoid composition in especially pure iron-carbon alloys. Impurities usually cause some change in the eutectoid composition and it seems likely that 0.83 per cent of carbon is the best value to use for commercial plain-carbon steels.

austenite before the eutectoid temperature is reached is called *proeutectoid cementite.*

Alloys that contain less than 0.04 per cent of carbon will transform without the formation of pearlite. These very low-carbon



FIG. 68*a*.—Ingot iron (almost pure ferrite). (*Courtesy of the Metals Research Laboratory, Carnegie Institute of Technology.*)

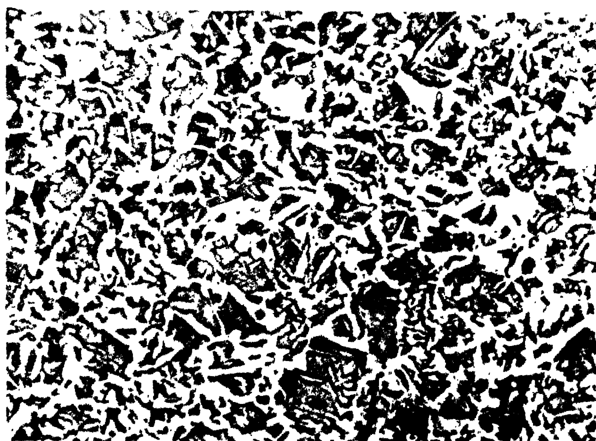


FIG. 68*b*.—Hypoeutectoid steel (0.30 per cent carbon). (*Courtesy of the Metals Research Laboratory, Carnegie Institute of Technology.*)

alloys would be classed as irons rather than as steels. On a basis of their metallographic constituents after being very slowly cooled through the critical region, steels are classed into three groups: ***hypoeutectoid steels,*** which contain less than 0.83 per cent of carbon and are composed of proeutectoid ferrite and pearlite after trans-

formation; *eutectoid steels*, which contain exactly 0.83 per cent of carbon and which transform entirely into pearlite; and *hypereutectoid steels*, containing over 0.83 per cent carbon, which transform into proeutectoid cementite and pearlite. Typical microstructures



Fig. 68*c*.—Eutectoid steel (0.83 per cent carbon). (*Courtesy of the Metals Research Laboratory, Carnegie Institute of Technology.*)



Fig. 68*d*.—Hypereutectoid steel (1.0 per cent carbon). (*Courtesy of the Metals Research Laboratory, Carnegie Institute of Technology.*)

of an iron composed entirely of ferrite, and of the three classes of steels, are shown by the photomicrographs in Fig. 68, *a*, *b*, *c*, *d*.

When steels are *very slowly* heated from temperatures below 723°C., the reverse of the changes just described will occur. A

eutectoid steel, composed entirely of pearlite will change completely into austenite when heated above the eutectoid temperature. The 1.3 per cent carbon steel would be converted entirely into austenite if heated to slightly above 960°C.; it would be necessary to heat the 0.3 per cent carbon steel to a little above 800°C. to make it completely austenitic.

The temperatures at which the phase or magnetic changes, already described, take place in irons or steels on heating or cooling are frequently called critical points. The curve *GS*, above which all hypoeutectoid steels become completely austenitic, is called the A_3 line and the temperature at which a steel of fixed composition crosses the A_3 line is known as the A_3 point for that steel; thus, the A_3 point for the 0.30 per cent carbon steel is 800°C. The line *MO*, above which ferrite is paramagnetic, is known as the A_2 line and the A_2 point of the above steel is 770°C. The A_2 points for steels containing from 0.45 to 0.83 per cent of carbon are identical with the A_3 point because no ferrite exists in these steels above *OS* and austenite is paramagnetic. The line *PSK*, above which eutectoid pearlite transforms into austenite, is called the A_1 line. The A_1 point for any plain carbon steel is 723°C.

For hypereutectoid steels, A_1 and A_2 are identical. The ferrite in pearlite is the only ferrite in a hypereutectoid steel below A_1. Since all pearlite transforms to austenite at A_1, hypereutectoid steels will be paramagnetic above A_1. The temperature at which proeutectoid cementite begins to form on cooling and disappears by solution in austenite on heating, is named the A_{cm} point. These points are given by the curve *SE*, called the A_{cm} line on the diagram. For the 1.3 per cent carbon steel, A_1 and A_2 occur at 723°C. and A_{cm} at 960°C. For a eutectoid steel A_1, A_2, A_3, and A_{cm} are identical at point *S* (723°C.).

The Iron-graphite Diagram.—The recent investigations of Seltz, McDonald, and Wells[1] confirm the earlier less reliable evidence that iron carbide is unstable in solid iron-carbon alloys. These investigators find iron carbide unstable with respect to iron saturated with carbon (saturated austenite) at all temperatures below about 1200°C. (2190°F.); with respect to pure gamma iron and graphite, the carbide is unstable at all temperatures below about 809°C. (1490°F.). The former is the important fact, because the decomposition of cementite in the heat-treatment of an iron or steel

[1] Wells, *Trans. A. S. M.*, **26**, 289, (1938). Seltz, McDonald, and Wells, *Trans. A.I.M.E.*, **140**, 263, (1940).

would lead to the formation of graphite and saturated austenite. Since cementite is unstable, we must consider the iron-iron carbide diagram (Figs. 64, 65, 67) as a metastable equilibrium phase diagram. The stable equilibrium diagram for the iron-carbon system is the iron-graphite diagram. Wells[1] has drawn such a diagram which shows that the $S'E'$ solubility curve for graphite in austenite lies somewhat to the left of SE for cementite; *i.e.*, the metastable cementite is slightly more soluble than graphite in austenite. Furthermore, the eutectoid for ferrite and graphite falls at a slightly higher temperature and a lower carbon content than the eutectoid for ferrite and cementite.

Normally the rate of decomposition of cementite is extremely slow, and graphite does not form unless the steel or cast iron containing cementite is held for a considerable time at elevated temperatures or unless the alloy contains a constituent such as silicon, nickel, or aluminum (page 380), which accelerates the rate of cementite decomposition. The process of graphite formation from cementite is known as *graphitization.* For steels in general, the rate of cementite decomposition is so slow that graphite does not form in the processes of solidification, hot working, and heat-treating. The iron-iron carbide metastable equilibrium diagram is therefore the one that must be understood and used to explain the phenomena associated with the solidification, cooling, and heating of steels.

Heat-treatment of Steels

The following definition of the term *heat-treatment* has been widely adopted:[2] "An operation or combination of operations, involving the heating and cooling of a metal or an alloy in the solid state for the purpose of obtaining certain desirable conditions or properties. Note: Heating and cooling for the sole purpose of mechanical working are excluded from the meaning of this definition." Cooling from hot rolling, forging, or casting temperatures may, however, constitute a sort of heat-treatment because the properties of the final product will depend upon the rate of cooling which, at least in some cases, may be controlled. For many purposes such cooling does not develop the desired property or combination of properties and the ferrous material is subjected to a properly designed heat-treatment cycle.

[1] Wells, *op. cit.*
[2] "Metals Handbook," 1939 ed. p. 942.

To design a proper heat-treatment or to explain the results obtained by heat-treatment, it is necessary to have a thorough understanding of the foregoing discussion of the iron-iron carbide diagram plus a knowledge of the influence of the rate of cooling or heating, composition, grain size, etc., upon the critical point transformations in ferrous materials.

Influence of Rate of Cooling or Heating on Critical Points.—In the discussion of the iron-iron carbide diagram, it was emphasized

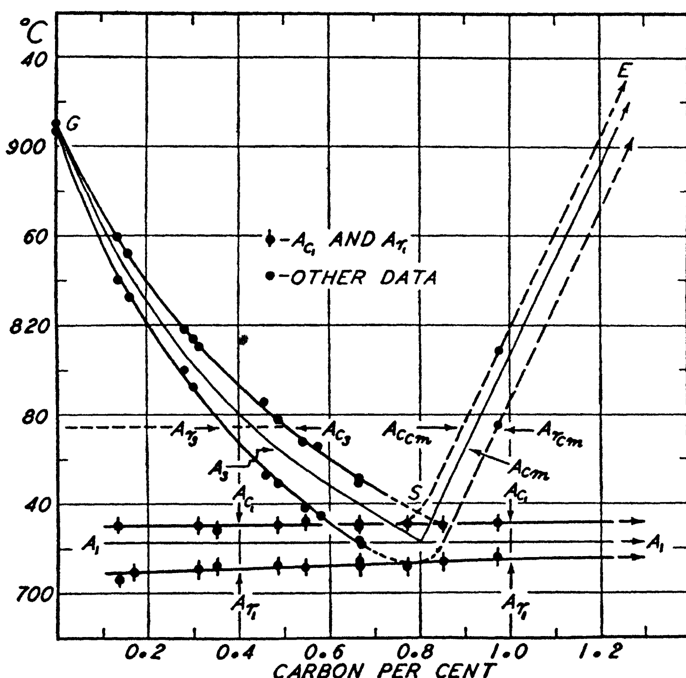


FIG. 69.—Critical points in iron-carbon alloys when heated or cooled at a rate of 0.5°C. per minute. (*Mehl and Wells, Trans. A.I.M.E.* **125**, 459 (1937).

that the transformations described took place at the indicated temperatures when the alloys were *very slowly* cooled or heated through the critical region; *i.e.*, it was assumed that the rate of cooling or heating was low enough to permit the establishment of equilibrium at all times. Actually some time is required for these transformations because such processes as nucleation, diffusion, and grain growth in the solid state are involved. Hence when steels are cooled through the critical region at practical rates, the critical point transformations occur at lower temperatures than are indicated on

the equilibrium diagram. The differences between the critical points on cooling a steel at a practical rate and those indicated by the equilibrium diagram naturally will increase with increase in the cooling rate. These differences also will depend on such factors as dimensions of the specimen, composition, and grain size.

To indicate that a critical point has been obtained on cooling, it is designated[1] by the symbol A_r. Thus, the A_3 point actually observed in cooling a hypoeutectoid steel is represented by A_{r3}. Critical points obtained on heating at practical rates are higher than the equilibrium A points and are indicated[1] as A_c points; and an A_1 point observed on heating would be indicated by A_{c1}. The actual relationships between the equilibrium critical points (A) and the critical points on cooling (A_r) or heating (A_c) at the rate of 0.5°C. per min. are well illustrated in Fig. 69. As the rates of cooling and heating are increased, there is of course a greater spread between A_c and A_r for a given steel.

When steels previously cooled to below the critical region are heated to temperatures even slightly above the critical region (above *GSE*, Fig. 67), transformations to austenite are in general quite rapid; *i.e.*, A_c transformations are not greatly delayed by increased rates of heating. On the other hand, when steels in the austenite condition at temperatures above *GSE* are rapidly cooled as in quenching,[2] the decomposition of austenite may be greatly repressed. Moreover, for a given steel, the character of the product may be controlled by the rate of cooling in the quenching operation, the temperature to which the steel is quenched, and by reheating the initial product of austenite decomposition in a process known as *tempering* or *drawing*. The phenomena associated with the decomposition of austenite and the tempering of the initial products are extremely important, but until recently they were little understood. Through the investigations of E. C. Bain[3] and R. F. Mehl[4] and their associates, the whole subject has been nicely elucidated and will now be discussed using a eutectoid steel as an example.

[1] This notation for the critical points was invented by early French metallurgists. A_r = arrest on cooling; r is from *refroidissement* (cooling). A_c = arrest on heating; c is from *chauffage* (heating).

[2] By quenching we mean rapid cooling by immersion in liquids or gases, or by contact with metal. See "Metals Handbook," 1939 ed., pp. 204, 323.

[3] BAIN, *et al.*, *Trans. A.I.M.E.*, **90**, 117 (1930); **100**, 13 (1932); *Trans. A.S.M.*, **20**, 385 (1932); **24**, 225 (1936).

[4] MEHL, *et al.*, "Symposium on Hardenability of Alloys," A.S.M. (1938)· *Trans. A.S.M.*, **29**, 813 (1941); *A.I.M.E. Preprint* (February 1942).

Austenite Transformation at Constant Subcritical Temperatures. Bain studied the products formed and the rate of transformation when austenite of eutectoid composition was suddenly quenched to a subcritical temperature and then held at constant temperature until the transformation was complete. At each temperature a finite time, called an induction period, elapses before decomposition products could be detected. After beginning, the transformation proceeds at a definite rate and becomes essentially complete in a characteristic period of time. The length of the induction period, the time required for transformation, and the character of the product of austenite decomposition, all are dependent upon the temperature at which the specimen is held.

At temperatures only slightly below the eutectoid temperature (723°C., 1330°F.), the induction period is a relatively long one; as the temperature for isothermal transformation is decreased, the induction period decreases, passing through a minimum at about 560°C. (1040°F.), increases again to a maximum at about 250°C. (480°F.), and then decreases again at lower temperatures. The time required for completion of the transformation, once it has started, also depends upon the temperature.

The structural characteristics and the physical properties of the products of the isothermal transformation also depend in a striking manner upon the temperature.

Pearlite.—At temperatures between the eutectoid and 560°C., pearlite is the product formed in the austenite transformation. At the higher temperatures, coarser pearlite is formed. As the temperature is decreased, the pearlite produced becomes finer and finer and, below 560°C., the product can no longer be identified as pearlite.

Bainite.—If the isothermal transformation of austenite occurs in the range between 560°C. (1040°F.) and about 160°C. (320°F.), the product is a dark-etching, more or less acicular aggregate called *bainite.* Bainite is fairly hard, moderately ductile, and magnetic.

Martensite.—At temperatures below about 160°C., austenite changes to a white-etching, acicular structure called *martensite.* It is the hardest constituent of steels with the exception of pure cementite; it is magnetic but is not sufficiently ductile for most applications. It should be mentioned that the transformation of austenite to martensite appears never to go to completion. Some "retained" austenite always is present in martensite.

The Bain S Curve.—All the facts concerning the transformation of austenite in a eutectoid steel at constant subcritical temperatures are very conveniently shown by Fig. 70, commonly known as a "Bain *S* curve." Photomicrographs of the half-transformed specimens at various temperatures are shown between the curves, and of the final products of the transformation on the right. Brinell hardness numbers (BHN) and Rockwell "*C*" hardness values (RC) for the products also are given.

It should be mentioned that, although the *S* curve in Fig. 70 is for plain carbon eutectoid steel, similar curves may be drawn for plain carbon steels of other compositions and for steels containing other alloying constituents. The general effect of reducing the carbon content is to shift the *S* curve to the left, and alloying additions (with the exception of Co) shift the curve to the right.

Structures Obtained by Cooling Steel at Various Rates.—With medium rates of cooling or slow quenching of a plain carbon steel from above the critical region, the product of austenite transformation is pearlite if the steel is of eutectoid composition; pearlite and ferrite if the steel is hypoeutectoid; and hypereutectoid steels yield cementite and pearlite. The temperature at which austenite transformation begins yielding pearlite as a product is known as the A_r' point. This temperature depends upon the cooling rate, decreasing as the rate of cooling increases. At slow rates of cooling (curve *D*, Fig. 71) coarse pearlite is formed, but as the rate of cooling is increased, the pearlite becomes finer and finer (curves *C* and *B*). Finally, at a sufficiently high quenching rate, austenite does not transform to form pearlite (no A_r' point) but remains austenite until, at low temperatures, it transforms into martensite. The temperature at which austenite begins to change into martensite is known as the A_r'' point and the rate of quenching just sufficient to prevent transformation of austenite into pearlite is called the *critical cooling rate.* At rates of cooling greater than the critical rate, the austenite, of course, is changed to martensite. Bainite[1] never is formed when a plain carbon steel is quenched directly to low temperatures. At rates definitely slower than the critical rate, pearlite is formed; at rates definitely faster than the critical rate, martensite is the product of the transformation. Upon quenching at rates near or only slightly slower than the critical, a mixed struc-

[1] To form bainite it would be necessary to quench austenite faster than the critical rate to 160 to 560°C. (320 to 1040°F.) and then hold in this temperature range for transformation.

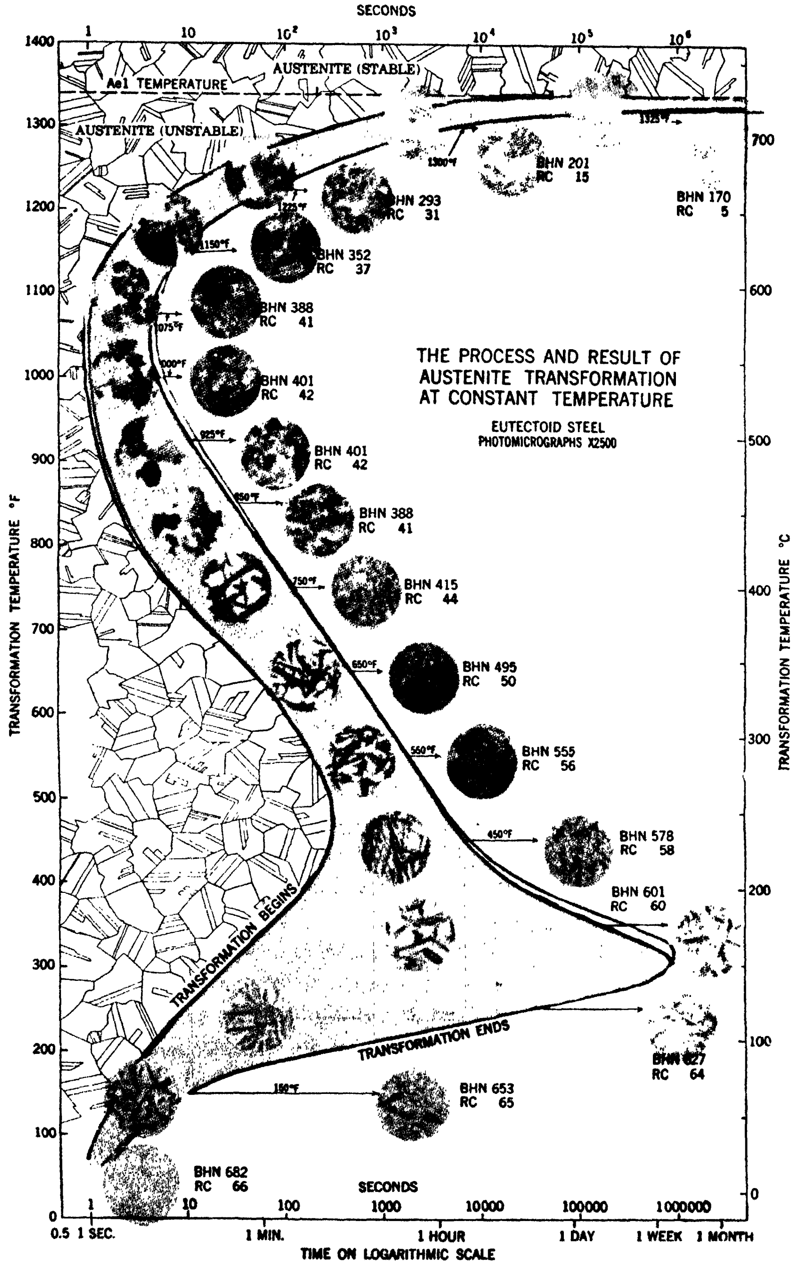


FIG. 70.—The Bain *S* curve for eutectoid steel. (*Courtesy of Dr. E. C. Bain.*)

ture, which is partly pearlitic and partly martensitic, is formed. For a eutectoid steel, the above relationships are well illustrated in Fig. 71.

Annealing and Normalizing.[1]—*Annealing* as used in heat-treatment is a rather comprehensive term but it usually implies heating to above the critical range for a time sufficient to convert the steel to austenite, followed by relatively slow cooling. The

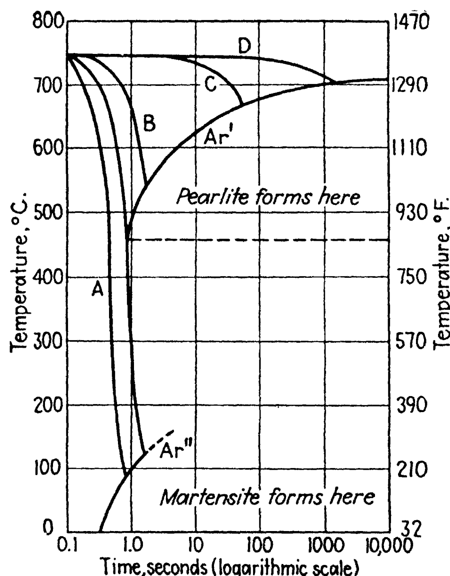


FIG. 71.—Cooling rates and products of transformation of austenite.

purpose of annealing may be one or more of the following: (1) to remove stresses; (2) to induce softness; (3) to alter ductility, toughness, electrical, magnetic, or other physical properties; (4) to refine crystalline structure; (5) to remove gases; or (6) to produce a definite microstructure.

Full annealing generally consists in heating an iron alloy to about 100°F. above the upper limit of the critical range, holding for not less than one hour for each inch of section of the heaviest objects being treated, usually followed by slow cooling in the furnace. Objects being treated, however, may be removed from the furnace and cooled in some medium that will cool the material more slowly than it would cool in air.

[1] "Metals Handbook," 1939 ed., pp. 3, 942.

Process annealing is the term applied to heating alloys of iron to a temperature below or close to the lower critical temperature (1020 to 1200°F.), followed by cooling as desired. This treatment is commonly used in the sheet and wire industries.

Patenting consists of heating iron alloys above the critical range followed by cooling below that range in air, or in molten lead or a molten mixture of nitrates or nitrites maintained between 800 and 1050°F. This treatment is used in the wire industry to precede further drawing.

Bright annealing is a process of annealing in the presence of reducing gases (page 345) so that surface oxidation is prevented or reduced to a minimum to obtain a bright surface on the annealed material.

Box annealing, *pot annealing*, and *close annealing* are processes for softening steel by slow heating to subcritical temperatures followed by slow cooling in a closed metal box or pot to prevent oxidation.

Normalizing is a term applied to the process of heating steel to approximately 100°F. above the critical temperature followed by cooling below this range in still air. Hypereutectoid steels may be normalized above A_{cm} but usually are annealed above A_{c1}. This is one of the simplest heat-treatments and, as the name implies, is intended to restore the structure and properties considered normal for the type of steel involved. It frequently is applied to castings, forgings, etc., to refine grain structure and to relieve stresses set up in previous operations. It is commonly applied after cold working, overheating, or any other operation resulting in nonuniform heating or cooling. It may be used to efface the effects of previous heat-treatments.

It should be mentioned that annealing and normalizing are essentially treatments for the purpose of softening and homogenizing steel. The rate of cooling in these operations is almost always slower than the critical rate and the structural constituents of annealed or normalized steels are those which would be expected from the equilibrium diagram for slow cooling (ferrite and pearlite for hypoeutectoid steels, etc., page 321). Only when quite thin sections are involved do these treatments lead to any appreciable hardening or increase in tensile strength.

Austenite Grain Size, Grain Growth, and Grain Refinement.—It has long been known that the grain size of a steel, other things being equal, has an influence upon its properties in the cooled condition and upon the properties that can be developed by heat-

treatment. As a result of recent investigations, we now have fairly precise methods for determining grain size, a knowledge of the relations between grain size and properties, and considerable information about the control of grain size in steelmaking, and methods for bringing about a certain amount of grain refinement after the steel is made.

Originally grain size was estimated by quenching and breaking a specimen and observing the fracture in comparison with fractures of standard samples. The estimates of grain size from fracture tests show a fair correlation with the results obtained by the microscopic examination of polished and etched specimens. If difficulty is encountered in obtaining sufficient contrast to make the boundaries of the original austenite grains plainly visible, resort may be had to the carburizing technique of the McQuaid-Ehn test[1] or other means. Standard A.S.T.M. austenite grain size numbers are in general use and corresponding grain size charts are available for comparison in making a determination of grain size. Each grain size number corresponds to a certain mean number of grains per square inch when the specimen is viewed at a magnification of 100 diameters as follows:

Grain size no.	−3	−2	−1	0	1	2	3	4	5	6	7	8	9	10	11	12
Grains per sq. in. at 100 ×	0.06	0.12	0.25	0.5	1	2	4	8	16	32	64	128	342	512	1024	2048

Most steels have a grain size in the range from 1 to 8. In general, heating a steel below the critical range, as in tempering or spheroidizing (page 337), does not lead to grain growth. However, when a steel in the austenitic condition is heated for a sufficient time above the critical region, austenitic grains grow in size. At temperatures only slightly above the critical, such as those used in annealing and normalizing, the rate of grain growth is very slow for some steels. As the temperature is increased a temperature will be reached at which grain coarsening will become quite rapid. This temperature, known as the *coarsening temperature*, is an inherent property of the composition, previous history, and method of manufacture of steel. In general, killed steels (page 307) are inherently finer grained and

[1] For a more detailed discussion of grain size determination, grain refinement, and the influence of grain size on physical properties, see "Metals Handbook," 1939 ed., pp. 750–767; Camp and Francis, 5th ed., pp. 844–853; Heyer, "Engineering Physical Metallurgy," pp. 228–242, D. Van Nostrand Company Inc., New York (1939).

have higher coarsening temperatures than unkilled steels, especially those which have been killed with aluminum.

Annealed and normalized products having a fine austenitic grain size (Nos. 5 to 8) are inferior for rough machining, better for fine finish machining, and inferior in formability to coarser grained (Nos. 1 to 4) steels of the same composition subjected to the same treatment. After proper heat-treatment, fine-grained steels are shallower hardening (page 335), tougher, less liable to distortion, usually free from quenching cracks, less susceptible to grinding cracks, and possess lower internal stress and less retained austenite than corresponding coarse-grained steels.

Concerning grain refinement, recent studies have led to the following conclusions:

1. Steels that already are fine grained and possess high coarsening temperatures are little changed in grain size by mechanical working or heat-treatment.

2. There is no tendency for grain refinement when steels are cooled from the austenitic state through the critical region.

3. When coarse-grained steels are heated through the critical range and the grain structure changes to austenite, a definite refinement in grain size usually results. However, to obtain the advantage of this refinement, temperatures above the critical must be kept below the coarsening temperature or grain growth will annul the effects of refinement.

4. There is lack of agreement on some of the factors that govern grain size and coarsening temperatures.

5. Once austenite grains have formed, the only possibility of refinement, without going through a heat-treating cycle, is by the hot-working processes of forging, rolling, pressing, upsetting, etc.

It is now understood that the real reason why austenite grain size has such an influence upon the properties of steels is because of its effect upon the rate of transformation of austenite. Other things being equal, a coarse-grained austenite will transform more slowly (have a lower critical cooling rate) than a corresponding fine-grained steel. The finer grained the steel, the higher must be the quenching rate to prevent the transformation of austenite to pearlite. Thus if two steels of identical composition and section, but of different austenite grain size, are quenched at the same rate from the same temperature above the critical region, one may transform to pearlite (the fine-grained one) and the other to martensite.

Hardening and Hardenability.—In a modern sense, hardening[1] is defined as the process of heating and quenching iron alloys from a temperature either within or above the critical temperature range for the purpose of producing a hardness superior to that obtained when the alloy is not quenched.

The hardening of steel by heating and quenching has been practiced as an art for many centuries. It is only in recent years, however, that a scientific basis for understanding and controlling the process has been evolved. Heating for hardening is no different essentially from heating for annealing or normalizing; *i.e.*, at the end of the heating period all, or at least a goodly portion, of the steel is in the austenitic condition. Hardening differs from annealing and normalizing in the manner of cooling; the rate of cooling being slow for annealing and normalizing and rapid (quenching) for hardening.

Quenching is defined as rapid cooling by immersion in liquids or gases or by contact with masses of metal. As the term actually is used, it means rapid cooling in any manner and includes cooling by direct jets of cold air, water, or other fluids against surfaces of articles too large to be cooled by immersion. For a more detailed discussion of the various factors that determine the rate of quench and the relative effectiveness of various quenching mediums, the reader is referred to larger treatises.[2] Needless to say, marked temperature gradients are established in any article during quenching because the interior of an article can lose heat only by transferring it to the surface. In quenching, the surface of an article is cooled at the most rapid rate, the cooling rate decreasing progressively as the distance from the surface increases. Quenching rates can be made such that the following cases are encountered in practice:

1. The cooling rate at the surface and throughout the piece may be slower than the critical cooling rate and austenite throughout transforms to pearlite.

2. The cooling rate throughout may be faster than the critical rate and austenite throughout the piece changes to martensite.

3. The cooling rate for some distance from the surface may be faster than the critical rate, leading to martensite formation, with the cooling rate in the central portion being slower than critical

[1] "Metals Handbook," 1939 ed., pp. 7, 660, 944, 948.

[2] CAMP and FRANCIS, 5th ed., pp. 865–876. "Metals Handbook," 1939 ed., pp. 328–335.

leading to pearlite formation. Intermediate portions will cool at or near the critical rate and a mixed structure (split transformation structures) partly martensitic and partly pearlitic will be obtained.

It is important to note that by cooling a given steel from above the critical temperature range very slowly, the maximum softness and ductility of which the steel is capable may be developed. By cooling the same steel from the same temperature very rapidly to room temperature it may be obtained in its hardest and most brittle form.

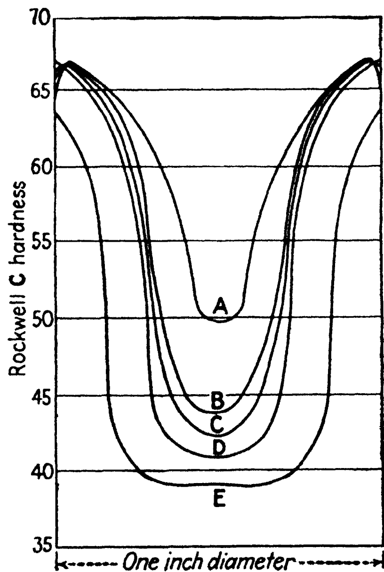


FIG. 72.—Hardenability curves.[2]

The hardening characteristics of a given steel may be determined by subjecting a specimen of standard size and shape, such as a 1-in. round, to a standard quench and then determining the hardness as a function of distance from a quenched end.[1] If the standard quench is by total immersion, the hardness is determined along a cross section, cut far enough from the end to eliminate end effects, at various distances along a diameter. In the latter case, a plot of hardness at various distances along a diameter yields a curve such as those illustrated in Fig. 72. The depth to which the hardening effect extends is called the *hardness penetration* or *depth of hardness.* A steel with high hardness penetration is said to be *deep hardening;* one with low hardness penetration is referred to as *shallow hardening.*

The hardenability of a steel becomes greater as the percentage of carbon is increased. It is further improved by the addition of such alloying elements as manganese, nickel, chromium, molybdenum, and vanadium, and by increase in the austenite grain size. All these factors improve the hardenability characteristics of a steel because they decrease the rate of austenite transformation and make it more easily possible to cool at a rate that will prevent pearlite formation and yield martensite when $A_{r''}$ temperatures are reached. To harden a piece of steel fully it must be quenched faster than the

[1] JOMINY and BOEGEHOLD, *Trans. A.S.M.*, **26**, 574 (1938).

[2] See note, page 385.

critical rate throughout so that all of the austenite that would form ferrite and pearlite at low rates of cooling will be transformed into martensite.

Local hardening, practiced for many years on gear teeth and the wearing surfaces of large castings, has been greatly extended in recent years. The part to be hardened is heated to above the critical temperature and quenched for hardening. When the oxyacetylene flame is used for heating, the process is known as flame hardening.[1] Local heating also may be accomplished by passing high currents through the portion to be hardened or by placing the part inside the coil of a high-frequency induction furnace.

Tempering (Drawing) and Spheroidizing.—Tempering or drawing consists in reheating hardened steel to some temperature below the lower critical temperature, followed by any desired rate of cooling. The pronounced stresses developed during and after drastic quenching for hardening may be great enough to cause cracks or even rupture of the hardened steel. For this reason hardened steels are seldom used without tempering, and tempering should be accomplished without appreciable time lapse after quenching. Tempering may be carried out at low temperatures, below 200°C. (400°F.), to relieve quenching stresses without appreciable loss in hardness, or it may be practiced at temperatures up to 650°C. (1200°F.) to give microstructures possessing various desirable combinations of hardness, strength, toughness, and ductility.

The naming of the microconstituents of steel obtained by tempering martensite has been the subject of considerable controversy. At low tempering temperatures 150 to 400°C. (300 to 750°F.) a dark-etching microconstituent is formed from martensite which consists of very fine carbide particles dispersed in ferrite. In the recent literature this constituent is called *tempered martensite* or *fine sorbite.* The name *troostite* was used in the past. If martensite is tempered at 400 to 700°C. (750 to 1290°F.), spheroidal cementite particles embedded in ferrite, visible at moderate magnification, are produced. This structure may be called *tempered martensite* or *coarse sorbite.* In the earlier literature this constituent is called *sorbite.* Finally, by prolonged tempering near to, or for a portion of the time slightly above, the lower critical temperature, coarse spheroidal cementite embedded in ferrite is produced. This structure is called *spheroidized cementite* or *spheroidite.* This structure

[1] "Metals Handbook," 1939 ed., p. 948.

also may be produced by tempering pearlite. Any heat-treatment that results in the production of spheroidized cementite or spheroidized carbides is known as spheroidizing.[1]

In concluding this section on heat-treatment, the reader must be reminded that the discussion has been confined to principles. As to the specific heat-treatments recommended for steels of various compositions for various applications, recourse must be had to the larger treatises.[2]



CASEHARDENING

For many applications, it is desirable to use a steel that has a tough or ductile interior or core and a hard wear- or corrosion-resisting surface. From the preceding section it is evident that this situation can be developed to a certain extent by carefully controlled quenching and tempering treatments. In certain applications, especially for automotive and other machinery parts, the desired differences between the properties of the surface and the core can be obtained only by having a higher concentration of an alloying element, such as carbon or nitrogen, in the outer portion of the piece than in the center. In such circumstances it is customary to select a steel that originally has the composition throughout that is desired in the core of the finished product. The surface composition is then changed, usually after at least the rough machining operations have been completed, by one of the following processes.

Case Carburizing.—This is the most commonly used process for altering the composition in the outer portion of a steel article. The steel is exposed, usually in the temperature range 840 to 950°C. (1550 to 1750°F.), to an environment that is capable of giving up carbon to the steel. At these temperatures, the steel is in the austenitic condition and the carbon yielded by the environment dissolves in the austenite, first at the surface and is then transferred away from the surface by diffusion. The surface layer in which the carbon concentration is appreciably higher than in the core is called the *case*, and the thickness of this layer, which becomes substantially harder than the interior, is known as the *case depth*. The surface carbon concentration will depend principally upon the carburizing medium and the temperature. The depth of penetration or case depth will depend upon the carbon concentration

[1] Metals Handbook, 1939 ed., pp. 4, 10.

[2] "Metals Handbook," 1939 ed. "S.A.E. Handbook," 1936 ed. BULLENS, "Steel and Its Heat Treatment," John Wiley & Sons, Inc., New York (1938)

maintained at the surface, the temperature, the composition of the steel, and the time.

In practice, the carburizing environment is supplied (1) by packing the steel article in a solid carbonaceous material (*pack carburizing*); (2) by exposing it to a carburizing gas such as methane, ethane, or carbon monoxide (*gas carburizing*); or (3) by immersing it in a fused salt bath containing cyanides and related compounds (*liquid carburizing* or *cyaniding*).

Very little forming, with the exception of lapping or light grinding, may be performed on the carburized part of a steel article. The principal forming and machining operations are accomplished before carburizing. It therefore is necessary to reduce distortion, scaling, etc., to a minimum during the carburizing process and the subsequent heat-treatment. To this end, parts frequently are annealed before carburizing and the heating, to temperature and during the process, is made as uniform as possible. Furthermore, much attention is paid to providing proper support for the article during the heating period and to its handling in all operations.

The selection of a steel for carburizing will, of course, depend upon the properties desired in the core and in the case, and these will depend upon the use to be made of the carburized part. Roughly, carburizing steels may be classified into three groups:

(1) Plain carbon steels, which usually contain carbon in the range 0.10 to 0.25 per cent. Normally, it is possible to exceed the critical cooling rate for the case in these steels only by a drastic quench in aqueous mediums and the core never is hardened unless the article is of extremely small cross section. Core strengths of about 100,000 psi, with adequate toughness, rarely can be exceeded with these steels. However, these steels are low in cost and their heat-treatment subsequent to carburizing is simple. If the drastic quench required for obtaining suitable properties causes distortion, resort must be had to steels of suitable alloying elements.

(2) Moderately alloyed carburizing steels, which contain from 1 to 2 per cent of alloying elements such as molybdenum, chromium, vanadium, and nickel, and carbon contents as high as 0.40 per cent. The alloying elements impart deeper hardening (page 335) characteristics to the core by decreasing the critical cooling rate. In these steels it usually is possible fully to harden by oil quenching; they are thus less liable to distortion. Core strengths as high as 175,000 to 190,000 psi with suitable toughness are obtainable if the alloy content is properly selected.

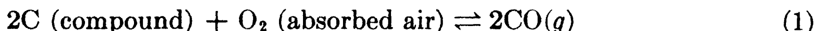
(3) Highly alloyed carburizing steels. To meet certain service requirements, steels containing over 2 per cent of such alloying elements as are listed above, together with carbon up to about 0.20 per cent, may be carburized. These steels may be hardened by a moderate oil quench to yield very desirable properties in the core. Their cost and the elaborate heat-treating cycles frequently required to develop their superior properties limit their use as carburizing steels.

Pack Carburizing.—In this process, the article to be carburized is placed in a carburizing box of proper design made of special heat-resisting alloy, cast steel, or steel sheet. The space between the piece and the box is filled with a solid carburizing compound. The layer of compound between the article and the box (about ½ in.) should be as uniform as possible to give a uniform transfer of heat from the outer surface of the box to the piece. The packed and covered box is then brought to the selected carburizing temperature and maintained there for a proper period. The temperature, time, and compound composition used will depend upon the surface carbon concentration and case depth desired. For example, with a typical commercial compound a case depth of 0.040 to 0.050 in. can be obtained at 925°C. (1700°F.) in an over-all carburizing time of nine hours. Of the nine hours, about five would be required for heating up the work and four hours would represent the time "at temperature." After carburizing, the work may be quenched directly, or it may be slowly cooled and thereafter subjected to proper heat-treatment.

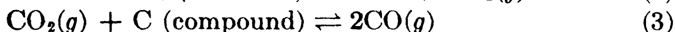
If certain parts of a piece are to be left uncarburized, they may be protected during the process in several ways. The parts may be protected by copper plating or by packing a noncarburizing material such as sand or fire clay about these portions in the box. If the work is slowly cooled after carburizing, the whole article may be carburized and the case then machined from the portion that is not to be casehardened.

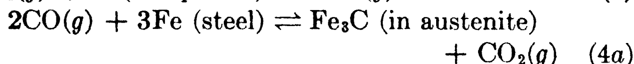
Commercial carburizing compounds of an almost infinite variety of compositions are available. Most of them contain some form of charcoal and alkali or alkaline earth carbonates, the latter acting as "energizers" to speed up the process. A typical composition is the following: 53 to 55 per cent of hardwood charcoal, 30 to 32 per cent of sized coke, 2 to 3 per cent of sodium carbonate, 10 to 12 per cent of barium carbonate, and 3 to 4 per cent of calcium carbonate. It seems certain that in pack carburizing, solid carbon is not transferred

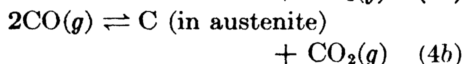
from the compound to the steel as such but by a mechanism that first involves the conversion of carbon to carbon monoxide. This gas then reacts on the surface of the steel to produce carbon that dissolves in the austenite and carbon dioxide, which again is converted to carbon monoxide by reaction with more carbon in the compound. The following reactions indicate the various steps in the process:


$$2C \text{ (compound)} + O_2 \text{ (absorbed air)} \rightleftharpoons 2CO(g) \quad (1)$$


$$BaCO_3 \text{ (activator)} \rightleftharpoons BaO + CO_2(g) \quad (2)$$


$$CO_2(g) + C \text{ (compound)} \rightleftharpoons 2CO(g) \quad (3)$$


$$2CO(g) + 3Fe \text{ (steel)} \rightleftharpoons Fe_3C \text{ (in austenite)} + CO_2(g) \quad (4a)$$


$$2CO(g) \rightleftharpoons C \text{ (in austenite)} + CO_2(g) \quad (4b)$$

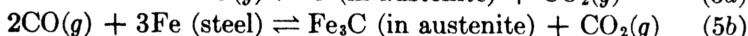
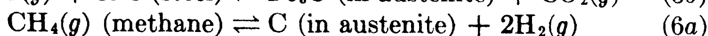
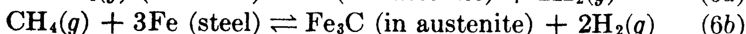
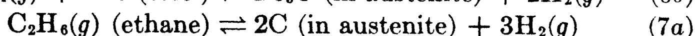
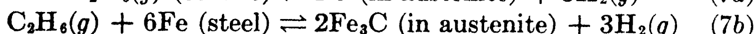
The carbon dioxide produced in the carburizing reaction (4*a*) or (4*b*) will again be converted to carbon monoxide by Eq. (3). Whether one writes Eq. (4*a*) or (4*b*) as the direct carburizing reaction will depend upon whether one considers that carbon is dissolved in austenite as free carbon or as iron carbide. Obviously, pack carburizing is very similar to the early processes for making "cement" steel and "blister" steel (page 277).

Gas Carburizing.—This process has increased in popularity in recent years, especially for the production of light cases, cases on small articles, and cases of carefully controlled surface carbon concentration. The process also can offer the advantages of cleanliness, speed, and automatic operation. However, for successful and economical operation of the gas carburizing process, there must be a large enough volume of work to keep the relatively expensive equipment busy, and a trained technical staff must be available.

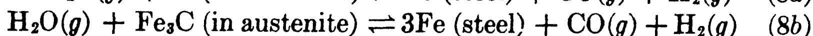
The common carburizing gases are methane, ethane, propane, butane, and carbon monoxide. We already have seen that it is carbon monoxide that actually yields carbon to steel in pack carburizing. Compared to the other gases, carbon monoxide is not a very active carburizing gas and it therefore is seldom used as such in gas carburizing; it may however be present as a constituent in many practical carburizing gases. The carburizing power of methane, ethane, propane, and butane increases in the order named, but these gases in the pure state are never used in practice. These pure gases would deposit so much soot (carbon) on the surface of

the work that the rate of carburization would be slow indeed. Methane and ethane usually are obtained as natural gas (75 to 85 per cent of methane, 5 to 20 per cent of ethane). Before use, natural gas is diluted with sufficient prepared lean gas or with spent gas from the process that the carburizing gas entering the process contains only 40 to 50 per cent of natural gas. Propane and butane usually are obtained relatively pure as liquids in cylinders under pressure. These then are mixed with large volumes of dilute gases for use in carburizing. Manufactured gas is so variable in composition, so low in hydrocarbons, and so high in carbon dioxide and water vapor, that it seldom is used for carburizing. To be made suitable, it usually must be dried and then enriched with a hydrocarbon such as propane.

The carburizing reactions may be written as follows:


$$2CO(g) \rightleftharpoons C\text{ (in austenite)} + CO_2(g) \qquad (5a)$$

$$2CO(g) + 3Fe\text{ (steel)} \rightleftharpoons Fe_3C\text{ (in austenite)} + CO_2(g) \qquad (5b)$$

$$CH_4(g)\text{ (methane)} \rightleftharpoons C\text{ (in austenite)} + 2H_2(g) \qquad (6a)$$

$$CH_4(g) + 3Fe\text{ (steel)} \rightleftharpoons Fe_3C\text{ (in austenite)} + 2H_2(g) \qquad (6b)$$

$$C_2H_6(g)\text{ (ethane)} \rightleftharpoons 2C\text{ (in austenite)} + 3H_2(g) \qquad (7a)$$

$$C_2H_6(g) + 6Fe\text{ (steel)} \rightleftharpoons 2Fe_3C\text{ (in austenite)} + 3H_2(g) \qquad (7b)$$

These reactions, especially (5) and (6), are definitely reversible reactions at carburizing temperatures. Pure CO_2 would decarburize steel to form CO by reversing reaction (5) and pure H_2 would decarburize steel by forming CH_4, the reverse of equation (6). Water vapor also is decarburizing, removing carbon from steel by the reaction


$$H_2O(g) + C\text{ (in austenite)} \rightleftharpoons Fe\text{ (steel)} + CO(g) + H_2(g) \qquad (8a)$$

$$H_2O(g) + Fe_3C\text{ (in austenite)} \rightleftharpoons 3Fe\text{ (steel)} + CO(g) + H_2(g) \qquad (8b)$$

Whether or not a gas mixture will be carburizing or decarburizing to a steel will depend upon (1) the gas composition, (2) the temperature, (3) the carbon content of the steel, and (4) the total pressure on the gas mixture. For example, at 900°C. (1650°F.) and 760 mm. Hg, total pressure, a mixture of CO and CO_2 containing about 91 per cent of CO will be in equilibrium with austenite containing 0.40 per cent of carbon. A CO-CO_2 mixture containing over 91 per cent of CO would be carburizing and a mixture containing less than 91 per cent of CO would be decarburizing to this steel at 900°C. and

760 mm. Hg, total pressure. As the temperature is increased, the percentage of CO in a CO-CO_2 mixture must be increased to give equal carburizing power. For more detailed information on casehardening by carburizing, the reader is referred to the abundant literature on the subject.[1]

Nitriding.[2]—The modern process for casehardening by nitriding dates from about 1920. The steel articles, usually finish-machined and free of rust and other surface dirt, are packed in a container provided with temperature control, to which ammonia gas can be admitted at a controlled rate. The temperatures employed usually lie in the range 480 to 540°C. (900 to 1000°F.) and it should be noted that these temperatures are below the critical temperature range for iron-carbon alloys. When ammonia enters the nitriding chamber, it undergoes partial dissociation, the extent of decomposition depending upon the temperature and the rate of flow. In practice, conditions usually are regulated to give about 30 per cent dissociation.

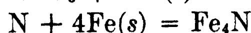
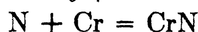
Iron nitride, Fe_4N (possibly also Fe_3N and Fe_2N), is not very stable, but it can be formed to a certain extent by the reaction of iron with ammonia or with atomic nitrogen. The nitrides of various alloying elements such as Al, Cr, Si, Mn, and Mo, are much more stable than iron nitride, and all nitriding steels (called nitralloys) contain several of these elements. It seems certain that the principal casehardening effect in nitriding is due to the formation of these more stable nitrides.


$$2NH_3 \rightleftharpoons 2N + 3H_2$$

$$2NH_3 + 2Al = 2AlN + 3H_2$$

$$N + N = N_2$$

$$N + Al = AlN$$

$$2NH_3 + 8Fe(s) = 2Fe_4N + 3H_2 \qquad 2NH_3 + 2Cr = 2CrN + 3H_2$$

$$N + 4Fe(s) = Fe_4N$$

$$N + Cr = CrN$$

The more commonly used nitriding steels will contain 0.20 to 0.40 per cent of carbon, 0.90 to 1.50 per cent of aluminum, 0.90 to 1.4 per cent of chromium, 0.15 to 0.25 per cent of molybdenum. In special types chromium may be replaced by molybdenum, or vanadium may be substituted for aluminum. Although nickel does not form a stable nitride, it is used in some nitralloys to

[1] CAMP and FRANCIS, 5th ed., pp. 896–906. "Metals Handbook," 1939 ed., pp. 1034–1059. *Trans. A.S.M.*, **26**, 427–766 (1938).

[2] "Metals Handbook," 1939 ed., pp. 1071–1081. *Trans. A.S.S.T.*, **16**, 67 (1929).

strengthen and harden the core. Furthermore, sulfur may be added to improve the machining properties.

It is possible by nitriding to develop greater case hardness, better wear resistance, better corrosion resistance, and better hardness retention at elevated temperatures than can be obtained by carburizing. The process suffers in comparison to carburizing on a basis of cost and because special alloy steels are required. Nevertheless, nitriding does find application in the production of machine parts that must have especially high wear resistance at elevated temperatures such as automobile and airplane valves and valve parts, piston pins, camshafts, and cylinder liners. It also finds some application in the production of ball- and roller-bearing parts, parts to withstand high-pressure steam service, die-casting dies, wire-drawing dies, etc.

The usual core depth produced in nitriding is only 0.01 to 0.02 in.; 0.04 in. certainly represents a maximum value that could be obtained by nitriding for 100 hr. or more.

√**Cyaniding and Liquid Carburizing.**[1]—The practice of case-hardening by bringing heated iron or low-carbon steel into contact with cyanides (prussiates) has been used for many years. In the earliest practice powdered cyanides were used in the blacksmith's forge; in modern practice cyaniding or liquid carburizing is accomplished by immersing the steel article in a bath of fused salts. The ordinary bath usually consists of 20 to 50 per cent of sodium cyanide mixed with sodium carbonate, or with sodium carbonate and sodium chloride. Recently various "activated" bath compositions have been developed which, although not greatly superior to the ordinary baths for the production of a very thin case, are decidedly superior when a fairly deep case is required. Besides sodium cyanide, the activated baths will contain such substances as the chlorides or cyanides of calcium or barium.

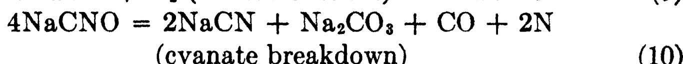
In liquid-bath carburizing or cyaniding, nitriding and carburizing are accomplished simultaneously. The normal temperature range employed is 730 to 900°C. (1350 to 1650°F.). The lower temperatures in this range favor nitriding and the higher temperatures carburizing. In activated baths, carburizing is relatively more important than nitriding, the case containing 50 to 75 per cent less nitrides than when ordinary cyanide baths are used.

[1] "Metals Handbook," 1939 ed., pp. 1060–1067. CAMP and FRANCIS, 5th ed., pp. 891–896. BECKWITH, *Trans. A.S.M.*, **26**, 752 (1938).

The chemical reactions believed to be involved in the process are



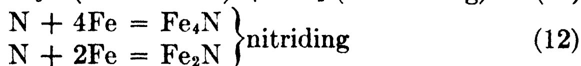
$$2NaCN + O_2 \text{ (limited amount)} = 2NaCNO \quad (9)$$



$$4NaCNO = 2NaCN + Na_2CO_3 + CO + 2N \text{ (cyanate breakdown)} \quad (10)$$



$$2CO + 3Fe = Fe_3C \text{ (in austenite)} + CO_2 \text{ (carburizing)} \quad (11)$$

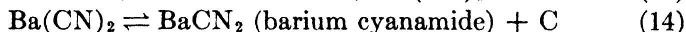


$$\left.\begin{array}{l} N + 4Fe = Fe_4N \\ N + 2Fe = Fe_2N \end{array}\right\} \text{nitriding} \quad (12)$$

In a bath activated with $BaCl_2$ or $Ba(CN)_2$ the following reactions also are involved:



$$2NaCN + BaCl_2 \rightleftharpoons 2NaCl + Ba(CN)_2 \quad (13)$$



$$Ba(CN)_2 \rightleftharpoons BaCN_2 \text{ (barium cyanamide)} + C \quad (14)$$



$$3Fe + C = Fe_3C \text{ (in austenite) carburizing} \quad (15)$$

The latter reactions explain why carburizing predominates over nitriding in activated baths.

Usually cyaniding is practiced for the production of shallow hard cases up to 0.01 in. in depth on machine parts. A case depth of 0.02 to 0.03 in. certainly represents the maximum practicable depth for this process. The deeper cases are more economically obtained by pack carburizing. The case depth will depend upon the composition of the steel, the bath composition, the temperature, and the time of immersion. When an S.A.E. 1015 (page 355) steel is immersed in a typical activated bath at 870°C. (1600°F.), one may expect a case depth of about 0.01 in. in 30 min.; 0.014 in. in 60 min.; and 0.018 in. in 90 min.

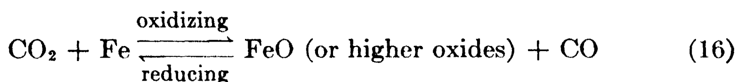
Cyanide salt baths also have an important application as mediums for heat treating, especially when it is important to prevent surface decarburization or oxidation during the heat-treating operation. For this reason, parts previously carburized by other processes frequently are heat-treated by use of fused cyanide baths.

Scaling, Decarburizing, and Bright Annealing[1]

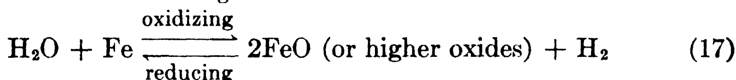
When iron or ferrous alloys are exposed to air at room temperature, oxygen reacts with the surface atoms of the metal to form iron oxides. If the air is moderately dry, the oxide film formed is

[1] For an excellent discussion of the equilibria involved in the production of protective atmospheres see "Controlled Atmospheres," American Society for Metals, Cleveland, Ohio (1942); Day and Austin, *Ind. Eng. Chem.*, **33**, 23 (1941).

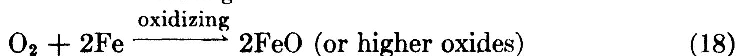
sufficiently nonporous and adherent effectively to keep more oxygen from coming to the surface after the film is several molecular layers in thickness. If the air is moist or dissolved in an aqueous medium, the oxide film is usually more porous and less adherent. In some such cases the attack may continue until all of the metal is converted into oxide or hydroxide. This type of attack is known as corrosion and will be discussed elsewhere (Chap. IX). At the higher temperatures involved in the mechanical working and heat-treating of iron and steel, air and various other oxidizing gases will form relatively thick oxide layers known as *scale*. All oxidizing gases also react with carbon to bring about decarburization, not only at the surface but also to some distance below the surface of the steel. Hydrogen, although it is a reducing gas, also will decarburize steel by uniting with the carbon to form methane.



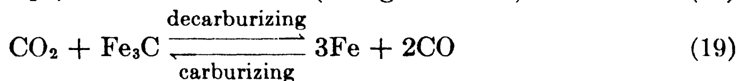
$$CO_2 + Fe \underset{\text{reducing}}{\overset{\text{oxidizing}}{\rightleftarrows}} FeO \text{ (or higher oxides)} + CO \qquad (16)$$



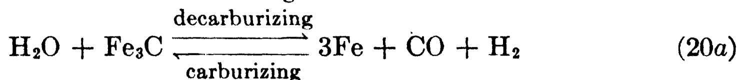
$$H_2O + Fe \underset{\text{reducing}}{\overset{\text{oxidizing}}{\rightleftarrows}} 2FeO \text{ (or higher oxides)} + H_2 \qquad (17)$$



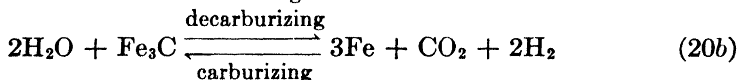
$$O_2 + 2Fe \xrightarrow{\text{oxidizing}} 2FeO \text{ (or higher oxides)} \qquad (18)$$



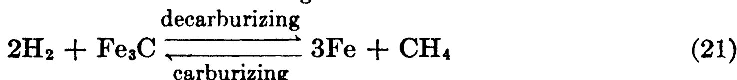
$$CO_2 + Fe_3C \underset{\text{carburizing}}{\overset{\text{decarburizing}}{\rightleftarrows}} 3Fe + 2CO \qquad (19)$$



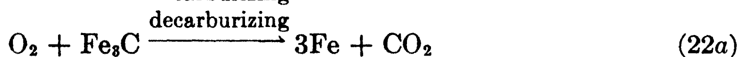
$$H_2O + Fe_3C \underset{\text{carburizing}}{\overset{\text{decarburizing}}{\rightleftarrows}} 3Fe + CO + H_2 \qquad (20a)$$



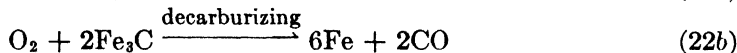
$$2H_2O + Fe_3C \underset{\text{carburizing}}{\overset{\text{decarburizing}}{\rightleftarrows}} 3Fe + CO_2 + 2H_2 \qquad (20b)$$



$$2H_2 + Fe_3C \underset{\text{carburizing}}{\overset{\text{decarburizing}}{\rightleftarrows}} 3Fe + CH_4 \qquad (21)$$



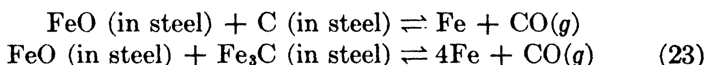
$$O_2 + Fe_3C \xrightarrow{\text{decarburizing}} 3Fe + CO_2 \qquad (22a)$$



$$O_2 + 2Fe_3C \xrightarrow{\text{decarburizing}} 6Fe + 2CO \qquad (22b)$$

All these reactions except those involving oxygen [Eqs. (18) and (22)] are reversible reactions at the temperatures involved in hot working and heat treating. Hence the direction of reaction will depend upon the composition of the gas mixture that comes in contact with the hot steel. In general, lower concentrations of the oxidizing

gases are required for decarburization than for oxidation. If a gas is oxidizing to steel, we may expect oxidation (scaling) and decarburization to go on simultaneously. However, a leaner gas might still be decarburizing even though it does not form scale. A high degree of oxidation of a steel must be accompanied by low carbon because of the requirements for equilibrium in the reaction:



$$\begin{aligned} \text{FeO (in steel)} + \text{C (in steel)} &\rightleftharpoons \text{Fe} + \text{CO}(g) \\ \text{FeO (in steel)} + \text{Fe}_3\text{C (in steel)} &\rightleftharpoons 4\text{Fe} + \text{CO}(g) \end{aligned} \qquad (23)$$

It would not be practical to provide an atmosphere other than air for the various processes for forming steel by hot working, and scaling invariably results in these processes. However, scaling losses in soaking pits and reheating furnaces can be reduced by applying our knowledge of the foregoing reactions to the control of the composition of the furnace gases.

The prevention of oxidation and decarburization in heat-treatment processes frequently becomes sufficiently important to justify special means for their control. One of the simplest examples of control is found in the process of box annealing, much used for steel sheets. The steel to be heat-treated is packed in cast-iron or steel boxes which may be sufficiently tight to prevent access of appreciable amounts of air. In some cases a protective atmosphere is admitted to the box or is caused to flow through the box during the heat-treatment process. In heat-treating furnaces, the atmosphere may be controlled by using an inert gas such as nitrogen or by using various gas mixtures of properly adjusted reducing and carburizing power. When control is sufficiently important, the heating up, heating at temperature, cooling or quenching, etc., parts of the heat-treating cycle, all may be carried out in mediums of controlled oxidizing-reducing and carburizing-decarburizing power. The use of fused salt baths containing cyanides as heat-treating mediums where it was important to prevent surface oxidation and decarburization has already been mentioned.

Wrought Iron and Open-hearth (Armco Ingot) Iron

Ingot iron, melted and refined by the basic open-hearth process, is a commercially pure iron. The carbon content rarely exceeds 0.02 to 0.03 per cent and the total impurities normally lie in the range 0.10 to 0.25 per cent. Due to the low-carbon content, the properties of ingot iron cannot be improved by heat-treatment and

its structure at room temperature is entirely ferritic. Its physical properties thus are the properties of ferrite, and one may expect low tensile strength (approximately 40,000 psi) and high ductility (approximately 35 per cent elongation and at least 20 per cent reduction in area in tensile tests). Ingot iron is used chiefly in the form of galvanized and enameled sheet.

Wrought iron also normally contains only 0.02 to 0.04 per cent of carbon. It usually is slightly lower in manganese and higher in phosphorus and silicon than ingot iron. One of the most distinctive features of wrought iron is the 1.0 to 2.0 per cent of ferrous silicate slag that it contains. In well-made wrought iron this slag is distributed as long slender fibers in the direction of rolling and is responsible for the good welding properties of the product. The slag also is undoubtedly responsible for the considerable difference between the longitudinal (tensile strength 47,000 psi; Charpy impact test, 17.5 ft.-lb.) and transverse (tensile strength, 34,500 psi; Charpy impact test, 5.0 ft.-lb.) properties. Owing to its ductility, toughness, and weldability, wrought iron finds some use for stay bolts, rivets, heavy chains and hooks, some grades of pipe, boiler tubes, ornamental ironwork, and other special applications.

The annual tonnage production of wrought iron is insignificant and that of ingot iron is small compared to the low-carbon steels.

Plain Carbon Steels

The *plain carbon steels*, also spoken of as *simple carbon*, *straight carbon*, and *ordinary carbon steels*, are those in which carbon is the only important element employed to control physical properties. They also contain small and usually specified amounts of various other metals and metalloids, such as manganese up to 1.0 per cent, silicon up to 0.2 per cent, and smaller amounts of phosphorus, sulfur, oxygen, nitrogen, and hydrogen. Occasionally they also contain small amounts of copper, chromium, nickel, aluminum, tin, lead, molybdenum, and arsenic. Some of these, especially manganese, are added intentionally to improve quality, but most of them arrive as constituents of steel-making raw materials.

Influence of Carbon Content.—The relation between carbon content and the microstructure of slowly cooled steels, and the influence of carbon on the structures and hardness that may be developed by heat-treatment have been discussed (page 318). Other variables being maintained constant, as the carbon content is increased up to about 0.85 per cent, there is an accompanying

regular increase in tensile strength, yield strength, and hardness, and a decrease in ductility as measured by reduction in area and elongation in tensile tests. The impact resistance of commercial hot-worked steel as measured by the Izod test also decreases with increase in carbon content. Further increase in carbon content above 0.85 per cent fails to increase the strength in the same ratio.

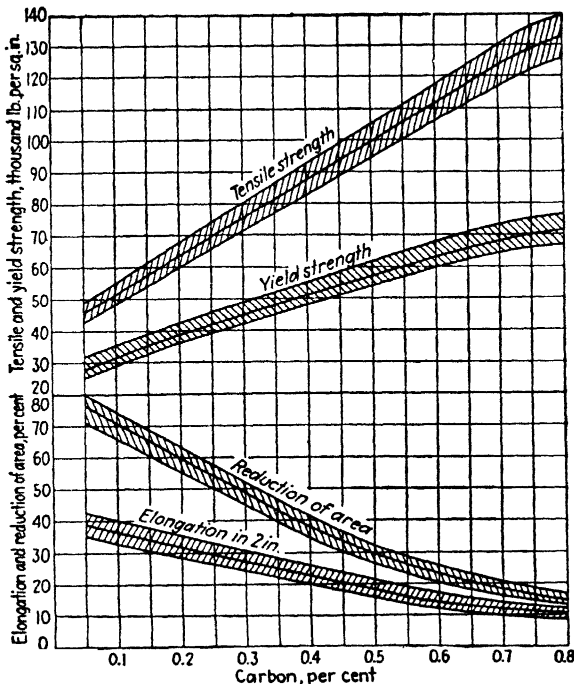


FIG. 73.—Effect of carbon on tensile properties of hot-worked carbon steels. (*From Sisco, "Modern Metallurgy for Engineers," Pitman Publishing Corporation.*)

Some of the properties to be expected in commercial hot-worked plain-carbon basic open-hearth steels or irons containing 0.30 to 0.60, per cent of manganese and 0.02 to 0.04 per cent of phosphorus are well illustrated in Fig. 73. Available data were subjected to statistical analysis in the preparation of the figure. The center line of the hatched area represents the properties to be expected most frequently. The boundaries of the hatched area represent the limits within which one may expect the properties to fall 95 per cent of the time. One would expect, therefore, that in the commercial testing of hot-rolled or forged basic open-hearth carbon steel

relatively few specimens would have properties represented by points outside the hatched areas.

The endurance limit (page 437) of hot-worked carbon steels increases with the tensile strength, but the ratio of endurance limit to tensile strength (endurance ratio) decreases somewhat as carbon content is increased, being 0.50 to 0.60 for irons and low-carbon steels and 0.35 to 0.45 for the high-carbon steels.

Influence of Minor Elements in Carbon Steel.—Phosphorus, sulfur, oxygen, nitrogen, and hydrogen usually are classed as harmful elements in steel. Although this may in general be considered a useful classification, their presence in proper amounts may be desirable in steels for certain special applications.

Phosphorus in appreciable amounts undoubtedly makes steel "cold short," *i.e.*, brittle when cold with a consequent low resistance to impact. The brittleness caused by phosphorus is marked if the amount of carbon plus phosphorus exceeds 0.30 per cent. Thus the effect is very pronounced in high-carbon and less important in low-carbon steels. In fixing specifications, a maximum of 0.10 to 0.12 per cent of phosphorus is permitted in low-carbon acid bessemer steels; in basic open-hearth rails, structural shapes, sheet, strip, etc., it is held under 0.045 per cent; in tool steels and other quality high-carbon and alloy steels the maximum permitted is 0.02 to 0.03 per cent of phosphorus. However, if the carbon is low, moderate amounts of phosphorus may be used to increase the tensile and yield strength and to increase the resistance to corrosion in certain environments. Some of the new high-strength low-alloy steels contain phosphorus to the extent of 0.10 per cent. Phosphorus forms the phosphide Fe_3P with iron, and, in the amounts usually present, this compound is completely soluble in both austenite and ferrite.

In the absence of manganese, sulfur combines with iron to form the sulfide FeS which is soluble in molten iron but quite insoluble in solid iron. As a consequence, FeS precipitates as an inclusion when iron solidifies. Owing to its low melting point, FeS imparts "hot shortness" to steel, a term used to describe brittleness at elevated temperatures which makes the steel susceptible to cracking during hot working. If sufficient manganese is present, most of the sulfur is converted to the more stable MnS which is less soluble than FeS in liquid iron. More of the sulfur is thus eliminated to the slag; that which remains in the steel as inclusions is in the form of a higher melting point compound that is less effective in

producing hot shortness. The only beneficial effect of sulfur in steel is to improve machinability. Free-cutting steels for automatic machining (screw stock) frequently contain as much as 0.15 per cent of sulfur, but for most steels a maximum sulfur content will be specified that lies in the range 0.01 to 0.065 per cent.

Until recently, the standard steel analysis consisted of the determination of carbon, manganese, sulfur, phosphorus, silicon, and those alloying elements specifically added. Owing to the differences in behavior of steels of the same standard analysis, it has been recognized that other elements in small amounts may exert considerable influence. This is especially true of oxygen and possibly also of nitrogen and hydrogen. All oxygen in steel undoubtedly is combined with other elements, hence not only the amount of oxygen but also the way it is combined is important. This whole subject of the relation of oxygen to carbon content, rimming action, deoxidation, grain size control, etc., has been discussed previously (page 301). The influence of the nitrogen and hydrogen content upon the properties of steel is little understood but is certain to be the subject of more investigation in the future.

Manganese has been used to overcome the deleterious effects of oxygen (deoxidation) and sulfur in steel ever since 1856. For this purpose it is an essential and beneficial constituent of nearly all grades of steel. In amounts up to 1.0 per cent it is added principally as a curative and corrective agent. However, even small amounts of manganese improve the tensile strength and also the hardenability by decreasing the critical cooling rate (pages 329, 335). Steels containing as much as 1.0 per cent of manganese and 0.50 per cent of carbon are susceptible to quench cracking and should not be quenched in water. There are a few important engineering steels, now widely used for railway rolling stock and bridges, which contain 1.00 to 1.90 per cent of manganese and must be classed as intermediate between plain carbon and low-alloy manganese steels.

As has been mentioned (page 301), silicon is widely used as a deoxidizer in the manufacture of medium- and high-carbon steels. Residual silicon in the form of the compound FeSi dissolves in ferrite and increases the tensile strength. However, steels that contain more than 0.50 per cent of silicon should be classed as alloy steels or irons.

The other elements that may be present in small amounts in plain-carbon steels do not exert a pronounced effect on physical

properties. Aluminum and titanium are used as deoxidizers, and copper to the extent of about 0.2 per cent, especially along with 0.1 to 0.14 per cent of phosphorus, imparts superior resistance to atmospheric corrosion.

Recently free-machining steels have been developed by the addition of 0.10 to 0.25 per cent of lead, incorporated in a highly dispersed state in low-carbon material.

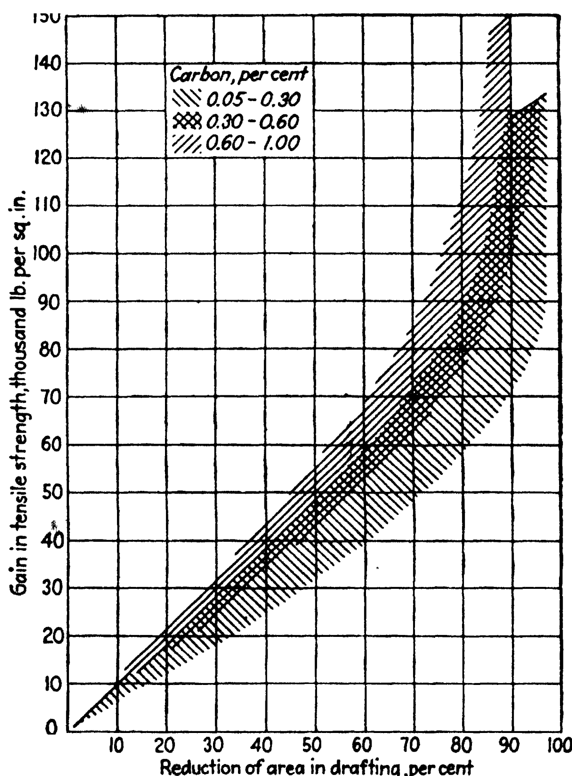


FIG. 74.—Effect of cold-working on tensile strength of carbon steel. (*Sisco, "Alloys of Iron and Carbon," Vol. II, McGraw-Hill Book Company, Inc.*)

Influence of Cold Work on Carbon Steels.—Cold working (cold rolling, stamping, pressing, drawing, etc.) is an important process because it is the most economical method for producing many classes of steel products in certain sizes and shapes and with the desired surface finish. Furthermore, it is possible to develop certain physical properties by cold work that cannot be secured by any other method. Sheet, strip, tubes, and bars are cold-worked

in large tonnages primarily to obtain certain sizes, shapes, and surface finishes, and are annealed before use. The anneal effaces any effect of cold work on physical properties.

On the other hand, much carbon steel, some in the form of sheet and strip but especially in the form of wire, is cold-worked and not annealed in order to preserve the physical properties induced in the operation. One of the most important cold-drawn products

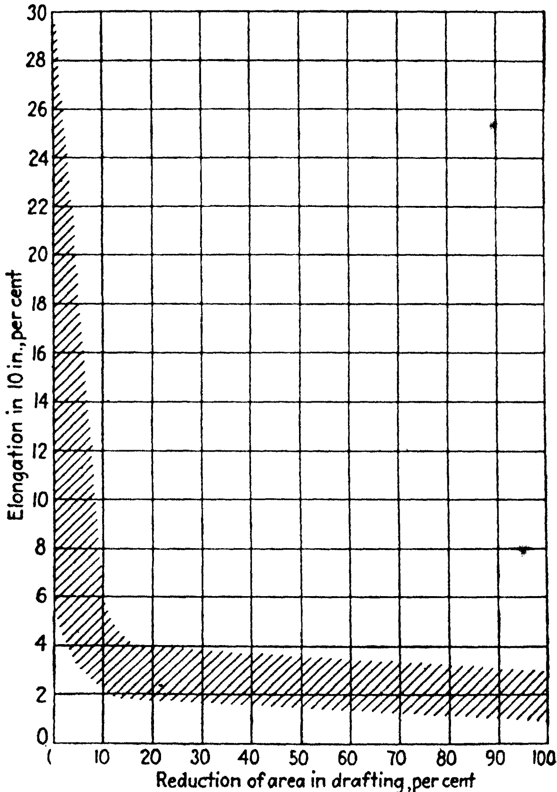


FIG. 75.—Effect of cold-working on the elongation of carbon steel wire. (*Sisco, "Alloys of Iron and Carbon," Vol. II, McGraw-Hill Book Company, Inc.*)

is steel wire containing 0.25 to 1.00 per cent of carbon used for music wire, springs, rope and cable wire, needles, etc. The principal effect of cold work is to bring about a rapid decrease in elongation, as is well illustrated in Figs. 74 and 75, and in Tables 57, 58, and 59. Table 58 shows that the effects of cold work are effaced by a subsequent anneal. It is well known that with sufficient cold work, the yield point of carbon steel disappears and the yield strength

becomes the same as the tensile strength. Annealing after cold work restores the yield point.

TABLE 57.—EFFECT OF COLD ROLLING ON TENSILE PROPERTIES OF A 0.14 PER CENT CARBON STEEL*

Property	Annealed	Reduced 30% by cold rolling	Reduced 60% by cold rolling
Tensile strength, psi	58,800	80,600	98,100
Yield strength, psi	34,400	75,300	96,700
Proportional limit, psi	27,500	15,600	10,100
Elongation in 4 in., %	41.7	22	10.5
Reduction of area, %	65.8	58	43

* From Sisco, "Modern Metallurgy for Engineers," Pitman Publishing Corporation, New York.

TABLE 58.—COMPARISON OF PROPERTIES OF HOT-ROLLED, COLD-ROLLED, AND ANNEALED 0.05 PER CENT CARBON STEEL*

Condition	Tensile strength, psi	Yield strength, psi	Elongation in 2 in., %
Hot-rolled strip	55,000	40,000	28
Cold-rolled, 50%	96,000	96,000	2
Annealed	44,000	33,000	38

* From Sisco, "Modern Metallurgy for Engineers," Pitman Publishing Corporation, New York.

TABLE 59.—EFFECT OF CARBON CONTENT ON STEEL REDUCED 60 PER CENT BY COLD ROLLING*

Carbon, %	Increase in tensile strength, %	Decrease in elongation, %
0.10	65	70
0.20	63	70
0.30	61	68
0.50	57	67

* From Sisco, "Modern Metallurgy for Engineers," Pitman Publishing Corporation, New York.

Cold working increases the endurance limit by about the same percentage as the tensile strength is increased. The endurance ratio is about 0.50 for cold-worked steel containing 0.05 per cent of

carbon, but drops to 0.25 to 0.35 for high-carbon wire. The resistance of carbon steel to impact is decreased by cold work.

S.A.E. Classification of Carbon Steels.—Although various professional societies and standardizing bodies have adopted standard specifications for steels for certain uses and have made standard classifications, those adopted by the A.S.T.M. and the S.A.E. are in most general use. Of these the S.A.E. classification and numbering system is most convenient. In this system, each carbon steel is designated by a series of four digits (1xxx); the first digit being 1 for all carbon steels.

Type of Steel	Number
Carbon steel	1xxx
Plain carbon	10xx
Free cutting (screw stock)	11xx
Free cutting (manganese)	X13xx

The last two digits are used to indicate the carbon content in "points" or hundredths of 1 per cent. Thus, S.A.E. 1040 is a plain carbon steel containing approximately 0.40 (0.35 to 0.45) per cent of carbon. For each S.A.E. steel, permissible ranges in the content of manganese, phosphorus, and sulfur are specified.[1] S.A.E. 1112 is a free-cutting steel containing approximately 0.12 (0.08 to 0.16) per cent of carbon and 0.10 to 0.20 per cent of sulfur. X1330 is a manganese free-cutting steel containing 0.25 to 0.35 per cent of carbon, 1.35 to 1.65 per cent of manganese, and 0.075 to 0.15 per cent of sulfur.

Carbon Steels as Engineering Materials.—In this section, the principal uses for various grades of carbon steel will be mentioned and the extent to which heat-treatments are used to obtain desirable properties will be indicated. For a description of the heat-treatments recommended for various grades in their various applications, the reader must consult the larger treatises.[2]

S.A.E. 1010–1025.—Enormous tonnages of these low-carbon steels are produced annually in the form of sheet, strip, rod, plate, pipe and other tubular products, wire, and structural shapes. With the exception of carburizing, annealing of cold-worked material, and occasional normalizing and quenching to improve machinability, these steels are rarely heat-treated because heat-treatments

[1] "S.A.E. Handbook," Society Automotive Engineers, Inc., New York. "Metals Handbook," 1939 ed.

[2] "S.A.E. Handbook." "Metals Handbook," 1939 ed. BULLENS, *op. cit.*

by direct quenching do not appreciably increase their hardness and strength. As has been mentioned (page 352), the hardness and strength of these low-carbon steels can be increased about 20 per cent by cold working.

S.A.E. 1010, containing as low as 0.05 per cent of carbon, is widely used in the form of sheet for the production of auto bodies and fenders by deep-drawing operations. Most tin plate, galvanized sheet, enameling sheet, fence wire, nails, much pipe, and other tubular products are made from this grade of steel. For most of these products a good surface finish is required; hence, most of it is of the "rimmed" (page 308) variety. However, killed steel of this grade is used for some applications.

S.A.E. 1020 and 1025 without heat-treatment find extensive use as boiler plate, pipe, and in the form of lower strength structural shapes. These grades are readily brazed, welded, and drawn, although they are not so suitable for deep drawing as S.A.E. 1010. These are standard carburizing grades of plain carbon steel for the production of fan blades, camshafts, wrist pins, and numerous forged and automatic parts where high strength is not essential. The higher manganese S.A.E. X1020 also is a carburizing grade, possessing better machining and hardening properties than S.A.E. 1020.

S.A.E. 1030–1050.—These medium-carbon steels are heat-treated for many of their applications because of the desirable strength, ductility, hardness, machinability, or other properties that can be induced by proper treatment. S.A.E. 1030 is used for forged, machined, or cold-worked parts requiring higher physical properties than are possessed by the low-carbon steels. It is suitable for casehardening when the section is large and when core hardness is desired. Without appreciable heat-treatment, this grade is used for seamless tubing and higher strength plain-carbon structural shapes. S.A.E. 1035 is suitable for small and medium-sized forgings. In the form of wire and rod it is used for shafting, axles, connecting rods, brake levers, gears, etc. Some hard-drawn wire for coiled springs is also made from these grades. For these same applications S.A.E. 1050 is frequently used when the sections are large.

In general these medium-carbon steels are an extremely important class of materials for the production of a large number of machinery and automotive parts. Without extensive heat-treatments, steels of this group find application in the form of

structural shapes, concrete reinforcing bars, and lightweight rails.

S.A.E. 1060–1095.—These, together with a few steels of even higher carbon content, may be classed as plain high-carbon tool and

TABLE 60.—SOME USES FOR HIGH-CARBON STEELS

Use	S.A.E. number							
	1060	1065	1070	1075	1080	1085	1090	1095
Bumper bars	..	..	..	..	..	x	x	x
Dies, drop forging	x	x	x					
Dies, metal cutting	..	..	..	..	x	x	x	x
Disks, clutch	x	..	x	..	..	x		
Disks, cultivator	..	..	..	x				
Disks, harrow, plow, seeder	..	..	..	..	x	..	x	x
Mower knives	..	..	..	..	..	x		
Plow beams and shares	..	..	x	x	x			
Railway car wheels	x	x	x	x	x	x		
Railway rails (heavy)	x	x	x	x				
Rake teeth	..	..	..	..	..	..	x	x
Saws, circular	..	..	..	..	x	x	x	
Saws, band	..	..	x	x	x			
Shovels	..	..	..	..	x			
Springs, clutch	x							
Springs, coil	..	x	x	x	x			
Springs, cushion	x							
Springs, leaf	..	..	..	..	..	x	x	x
Springs, seat	..	..	..	..	..	..	x	x
Springs, valve	x	x						
Tools, carpenters'	x	x	x	x	x	x	x	x
Tools, cold chisels	..	..	x	x	x			
Tools, hammers	x	x	x	x	x			
Tools, machinists' (general)	..	..	x	x	x	x	x	x
Tools, punches	..	..	..	..	x	x	x	x
Tools, rock drills	..	..	..	..	x	x	x	x
Wire, hard-drawn, spring	..	x						
Wire, music	..	..	..	..	..	x		
Wire, structural	..	..	..	x	x	x		

die steels because they are used extensively for tools and dies where high hardness is the chief requirement. The principal uses for these steels are indicated in Tables 60 and 61.

Medium- and high-carbon steels are rarely used in the quenched and untempered condition because of their brittleness. By tempering, this brittleness may be relieved. If the tempering tempera-

ture is high enough to change the particle size of the carbide, the strength and hardness decrease, and the ductility increases in the tempering process. The higher the tempering temperature, the more pronounced are these effects. The conditions for quenching and tempering must therefore be adapted to the grade of steel and to the properties desired for a particular application.

TABLE 61.—SOME USES FOR CARBON STEELS CONTAINING 1.0 PER CENT OR MORE OF CARBON

Uses	Carbon %							
	1.0	1.1	1.2	1.3	1.4	1.5	1.6	Over 1.6
Dies, metal cutting	x	x	x					
Dies, thread cutting	..	x	x					
Dies, wire drawing	..	..	..	x	x	x	x	x
Files	..	..	x	x				
Razor blades	..	..	x					
Saws, for cutting steel	..	..	..	..	..	x	x	
Springs	x	x	x					
Tools, carpenters'	x	x	x					
Tools, lathe	x	x	x					
Tools, machinists' (general)	x	x	x					
Tools, stone cutting	..	..	..	x	x			
Tools, wood cutting	..	x	x					

LOW-ALLOY STEELS

If an element other than carbon is added to steel, not primarily for deoxidation (page 302), in sufficient amount to cause a desired specific effect, the product is called an alloy steel. Many metals and some nonmetals have been alloyed with carbon steel and in many cases the properties of the alloys have been studied. The most common alloying elements are Mn, Si, Ni, Cr, V, W, Mo, Cu, and P. Of the more commonly used elements the ranges of percentages found in the low-alloy steels are shown in Table 62.

Since 1910 hundreds of alloy steels have been developed containing from one to a half-dozen alloying elements. Of these, several hundred low-alloy steels, and probably an equal number of high-alloy steels, are still being produced. The present number is undoubtedly too large; nevertheless, alloy steels have attained an extremely important place in our industrial civilization. Without

TABLE 62.—COMMON ALLOYING ELEMENTS IN LOW-ALLOY STEELS

Element	Percentage Range in Low-alloy Steels
Chromium	0.25–3.50
Copper	0.15–1.50
Manganese	1.00–2.00
Molybdenum	0.15–0.50
Nickel	1.00–5.50
Phosphorus	0.06–0.15
Silicon	0.50–5.00
Vanadium	0.15–0.25

them, the modern airplane and streamlined train would be impossible, and our automotive equipment would probably be twice as heavy and only half as efficient. The most convincing proof of the importance of alloy steels as engineering materials is found in the fact that year by year they constitute a larger percentage of our total steel production. About 75 per cent of the alloy steel produced is used by the aircraft and automotive industries. Any alloy steel costs more than a plain-carbon steel of equal carbon content and should be selected for a certain application only if, after considering such factors as weight, design, cost of fabrication, and expected life, the use of the alloy steel represents an economy.

Low-alloy steels may be roughly classified into two groups, namely, (1) the low-alloy low-carbon high-strength steels (sometimes called the "low-alloy structural steels") and (2) the low-alloy engineering steels. Of the latter group, some 70 or 80 have been included in the list of specified S.A.E. steels.[1]

Influence of Alloying Elements.—To be successful, an alloy steel must overcome one or more of the following disadvantages that are inherent in the plain-carbon steels: (1) The ductility of carbon steel decreases rapidly as carbon content is increased. (2) Optimum properties can be developed in carbon steels by heat-treatment only in small sections. (3) The physical properties of carbon steels deteriorate markedly with increase in temperature. (4) Plain-carbon steels are quite susceptible to chemical attack by the environment, especially at elevated temperatures.

In the low-alloy steels the primary effects of alloying elements are (1) to harden and strengthen the ferrite and (2) to make possible the development of more desirable properties, such as improved hardenability. Alloying elements also may influence properties by exerting an effect on grain size and by carbide formation. A few

[1] See "S.A.E. Handbook."

of the common alloying elements (especially Cr, Mo, W, and V) have strong carbide-forming tendencies. This property, however, becomes important chiefly in the high-alloy steels.

The Low-alloy Low-carbon High-strength Steels.—During the past 10 years the major steel companies have made available a variety of low-alloy "tailor-made" steels of "balanced" composition which have a yield strength almost twice that of low-carbon steel. These steels also possess good weldability, high ductility, and usually a superior resistance to atmospheric corrosion. These steels are produced in large tonnages and usually are given no heat-treatment except by controlling the cooling rate after hot rolling. In general they cost 15 to 50 per cent more than plain-carbon steels but, due to their higher yield strength, the size of sections can be reduced by 25 to 35 per cent with a resulting saving of 10 to 15 per cent in the cost of a structure. They are being used extensively for building railway rolling stock, streetcars, trucks, busses, and similar structures. In general, these steels will contain 0.08 to 0.40 per cent of carbon and will have yield strengths in the range 45,000 to 80,000 psi and tensile strengths from 65,000 to 100,000 psi. The percentages of the alloying elements in a few of these steels are given in Table 63.

TABLE 63.—LOW-ALLOY HIGH-STRENGTH STEELS

Trade name	Percentage of alloying element						
	Cr	Cu	Mn	Mo	Ni	P	Si
Cor-ten	0.50–1.50	0.30–0.50	0.10–0.50			0.10–0.20	0.50–1.00
Hi-steel		0.90–1.25	0.50–0.70		0.45–0.65	0.10–0.15	0.30 max.
Jal-ten		0.40 min.	1.25–1.75			0.40 max.	0.30 max.
Konik	0.07–0.30	0.10–0.30			0.30–0.50		
Man-ten		0.20 min.	1.25–1.70			0.04 max.	0.30 max.
RDS-1		0.50–1.50	0.50–1.00	0.10 min.	0.50–1.00	0.10 max.	
Yoloy		0.85–1.10	0.30–0.90		1.50–2.00		0.10–0.25

S.A.E. Low-alloy Steels.—There are two series of intermediate manganese steels: S.A.E. X13xx, which are the free-machining steels containing 1.35 to 1.65 per cent of manganese and 0.075 to 0.15 per cent of sulfur, and S.A.E. T13xx containing 1.60 to 1.90 per cent of manganese and 0.05 max. per cent of sulfur. The remainder of these S.A.E. low-alloy engineering steels may be classified under the headings: nickel steels (S.A.E. 2xxx), nickel-chromium steels (S.A.E.

3xxx), molybdenum steels (S.A.E. 4xxx), chromium steels (S.A.E. 5xxx and 5xxxx), chromium-vanadium steels (S.A.E. 6xxx), chromium-tungsten steels (S.A.E. 7xxx), and silico-manganese steels (S.A.E. 9xxx). As in the plain carbon steels, the last two digits in the S.A.E. number are used to indicate the carbon content in hundredths of a per cent. The second digit is used to indicate

TABLE 64.—S.A.E. LOW-ALLOY ENGINEERING STEELS

S.A.E., series	Range in percentage of alloying element			
	Chromium	Manganese	Molybdenum	
20xx	....	0.30–0.60		Nickel steels
21xx	....	0.30–0.60		
23xx	....	0.30–0.90		
25xx	....	0.30–0.60		
31xx	0.45–0.75	0.30–0.90		Nickel-chromium steels
32xx	0.90–1.25	0.30–0.60		
33xx	1.25–1.75	0.30–0.60		
34xx	0.60–0.95	0.30–0.60		
41xx	0.80–1.10	0.40–0.90	0.15–0.25	Molybdenum steels
43xx	0.30–0.80	0.50–0.80	0.15–0.40	
46xx	....	0.40–0.80	0.20–0.30	
48xx	....	0.40–0.60	0.20–0.30	
51xx	0.60–1.10	0.30–0.90		Chromium steels
521xx	1.20–1.50	0.20–0.50		
61xx	0.80–1.10	0.20–0.90	0.15 min.*	Chromium-vanadium steels
72xx	0.50–1.00	0.30	1.50–2.00†	Chromium-tungsten steels
92xx	....	0.60–0.90	1.80–2.20‡	Silicon-manganese steels

* Per cent of vanadium.
† Per cent of tungsten.
‡ Per cent of silicon.

the percentage of an alloying element. In all of these steels, maximum percentages for sulfur (usually 0.04 to 0.05 per cent) and for phosphorus (usually 0.03 to 0.04 per cent) are specified.[1] The range of percentage of the alloying element or elements in each of the S.A.E. series of steels is given in Table 64.

The S.A.E. low-alloy steels must be heat-treated to develop optimum physical properties. When properly treated, they combine high ductility with high strength. As has been mentioned, these steels are widely used in the construction of automotive equipment, aircraft, and various types of machines; especially for

[1] See "S.A.E. Handbook" for complete composition specifications.

highly stressed parts such as shafts, axles, gears, crankshafts, camshafts, and steering knuckles.

Heat-treated low-alloy steels usually will possess yield strengths 30 to 40 per cent higher, elongations 10 to 20 per cent higher, reductions in area 35 to 40 per cent higher, and impact resistances about 80 to 100 per cent higher than plain-carbon steels of the same tensile strength and hardness. These steels have lower critical cooling rates than plain-carbon steels. They are therefore deeper hardening (it is easier to harden large sections throughout), and oil quenching suffices to obtain high hardness and strength with less likelihoods of distortion and the development of high internal stresses.

For guidance in the selection of the best steel for a given application and the heat-treatment that will develop optimum properties, the reader should consult the larger treatises.[1]

Silicon Electrical "Steels."—Low-alloy steels containing up to 5.0 per cent of silicon and very low in carbon and other impurities find important use in the construction of transformers, motors, and generators. Silicon, by increasing electrical resistance and by promoting grain growth, gives an alloy in which eddy and hysteresis losses are small in alternating-current machinery. A typical high-grade transformer sheet will contain 1.0 to 5.0 per cent of silicon, manganese under 0.10 per cent, phosphorus under 0.02 per cent, sulfur under 0.02 per cent, and carbon under 0.05 per cent. The ordinary physical properties obviously are not very important in steels for this application.

High-alloy Steels

The many high-alloy steels may for convenience be divided into three classes: (1) high-speed tool, die, and valve steels, which are usually high in tungsten or chromium, or both, and sometimes contain appreciable amounts of vanadium and silicon; (2) special high-alloy steels for specific applications in which unique wear resistance, thermal expansion, magnetic or electrical characteristics, or other properties are highly important; (3) corrosion- and heat-resisting steels containing chromium in the range 10 to 30 per cent, or containing nickel or other alloying elements along with chromium. Of these high-alloy steels only those listed in Table 65 are included in the S.A.E. classification. Steels of the first class listed

[1] "S.A.E. Handbook." "Metals Handbook," 1939 ed. Williams, "What Steel Shall I Use," American Society for Metals, Cleveland, Ohio (1941).

above will be discussed in the next section along with other tool and die steels.

TABLE 65.—S.A.E. HIGH-ALLOY STEELS

S.A.E. no.	Percentage of alloying element				
	Tungsten steels				
	Carbon	Manganese	Chromium	Tungsten	
71360	0.50–0.70	0.30 max.	3.00–4.00	12.00–15.00	
71660	0.50–0.70	0.30 max.	3.00–4.00	15.00–18.00	
	Corrosion- and heat-resisting steels				
	Carbon	Manganese	Silicon	Chromium	Nickel
30905	0.08	0.20–0.70	0.75 max.	17.0–20.0	8.0–10.0
30915	0.09–0.20	0.20–0.70	0.75 max.	17.0–20.0	8.0–10.0
51210	0.12	0.60	0.50 max.	11.5–13.0	
X51410	0.12	0.60	0.50 max.	13.0–15.0	
51335	0.25–0.40	0.60	0.50 max.	12.0–14.0	
51510	0.12	0.60	0.50 max.	14.0–16.0	
51710	0.12	0.60	0.50 max.	16.0–18.0	

Special High-alloy Steels.—One of the oldest high-alloy steels is *Austenitic manganese steel* (*Hadfield manganese steel*) which contains 1.0 to 1.3 per cent of carbon, and 11 to 14 per cent of manganese. This steel may be hot-rolled into various shapes, but it work-hardens to such an extent that it cannot be machined readily. Cold shaping usually must be accomplished by grinding. Manganese, in the amounts present in these steels, forms solid solutions with both alpha and gamma iron. It forms the carbide, $(Fe, Mn)_3C$, probably a solid solution of Mn_3C in Fe_3C. Manganese lowers the A_3 point; with 13 per cent of manganese and no carbon, the alpha to gamma transformation temperature is 620°C. (1150°F.). The phase relations for these steels containing carbon are very similar to those for iron-carbon alloys except that all critical points are lowered. Furthermore, the presence of high percentages of manganese make all phase changes very sluggish. As a consequence these steels, at ordinary rates of cooling, consist largely of gamma solid solution (austenite) plus a little alpha solid solution and a

small amount of carbide. By reheating and quenching a completely austenitic structure may be obtained which possesses tensile strengths in the range 130,000 to 160,000 psi and a Brinell hardness of 180 to 220. Cold work causes a rapid increase in hardness to values as high as 550 Brinell. For this reason the high-manganese steels have exceedingly high abrasion resistance and find important use in the construction of grinders, crushers, crossovers, switches, frogs, steam-shovel buckets, and a variety of articles that must withstand pounding and abrasion. For these purposes the high-manganese steels will have several times the life of a high-carbon steel.

Nickel, like manganese, forms solid solutions with both gamma and alpha iron, lowers the A_3 critical point drastically and greatly decreases the speed of phase changes. As a consequence, highly important magnetic, electrical, and expansion characteristics may be obtained in iron-nickel alloys by proper selection of composition and heat-treatment (page 248).

Corrosion- and Heat-resisting Steels.—As has been mentioned, these steels contain chromium, either alone or together with nickel or other alloying elements. Only a few of these high-chromium and chromium-alloy steels have been included in the S.A.E. classification. However, a fairly comprehensive classification has been adopted by the American Iron and Steel Institute which includes the assignment of A.I.S.I. type numbers.[1] The limitations of space permit a discussion of only the most important types of these steels and the most essential facts concerning their constitution, properties, and behavior. For convenience this group of steels may be divided into three subgroups:

1. Steels containing 3.5 to 10.0 per cent of chromium with or without 0.5 to 4.0 per cent of molybdenum, nickel, silicon, or tungsten as additional alloying elements. These steels are more corrosion and heat resistant than the low-alloy steels containing chromium in the S.A.E. series 51xx, 521xx, 61xx, and 72xx. Silichrome, containing 0.5 per cent of carbon, 1.0 to 3.75 per cent of silicon, and 7.0 to 10.0 per cent of chromium, is resistant to the exhaust gases of engines at dull-red heat and is used for valves in automobile and airplane motors. Another steel of this group, containing 4.0 to 6.0 per cent of chromium, 0.40 to 0.75 per cent of silicon, 0.50 per cent of molybdenum, and about 0.10 per cent of carbon, has found extensive use in oil refinery equipment.

[1] CAMP and FRANCIS, 5th ed., p. 1007. HEYER, *op. cit.*, p. 477.

2. Steels containing more than 10 per cent of chromium and not more than 2.0 per cent of another alloying element. These steels find many applications because of their corrosion- and heat-resistant qualities as indicated below:

a. Low-carbon, high-chromium steels ("stainless irons") containing 12 to 18 per cent of chromium and less than 0.14 per cent of carbon. Martensitic steels of this class are used for turbine blades, pistons, valves, etc. In the ferritic state, steels of this group are quite ductile and may be cold-worked to produce parts for auto trim, interior work, etc. The resistance of these steels to high temperature oxidation may be improved by the addition of moderate amounts of aluminum; their machinability may be improved by the addition of sulfur, selenium, or molybdenum.

b. Steels containing 0.20 to 0.60 per cent of carbon and 12 to 17 per cent of chromium constitute the important group of stainless cutlery steels (martensitic).

c. A group containing 12 to 18 per cent of chromium and 0.70 to 2.0 per cent of carbon (martensitic) find considerable use as tool, die, and valve steels.

d. For superior oxidation resistance at high temperatures, steels have been developed with chromium contents in the range 20 to 30 per cent. If these steels are to be hot-worked, the carbon content is held under 0.50 per cent.

3. Steels containing more than 10 per cent of chromium and more than 2 per cent of one or more other alloying elements. These steels possess superior corrosion and heat resistance, desirable mechanical properties, and satisfactory weldability—a combination of properties that makes them exceedingly important engineering materials. By far the most important steel of this group is the famous 18 per cent chromium, 8 per cent nickel, low-carbon steel, known to metallurgists and other engineers as "18-8." The susceptibility to intergranular corrosion in 18-8 is offset in the "stabilized 18-8" steels by the addition of small percentages of molybdenum, titanium, or columbium. In 1939, 78,000 tons of 18-8 were produced in the United States, a fourfold increase over the production in 1929.

Constitution and Properties of Iron-chromium-carbon Alloys.—As is evident from Fig. 76, chromium dissolves completely in carbon-free iron to the extent of slightly over 30 per cent at ordinary

temperature, and to higher percentages at higher temperatures. The addition of chromium to iron drastically lowers the A_4 point. Up to about 7.0 per cent, the addition of chromium also lowers the A_3 point in iron; but further additions raise A_3 until at about 12 per cent of chromium A_3 and A_4 merge, yielding the "gamma loop" type of diagram which is characteristic of several of the binary systems in which iron is one component (iron with aluminum,

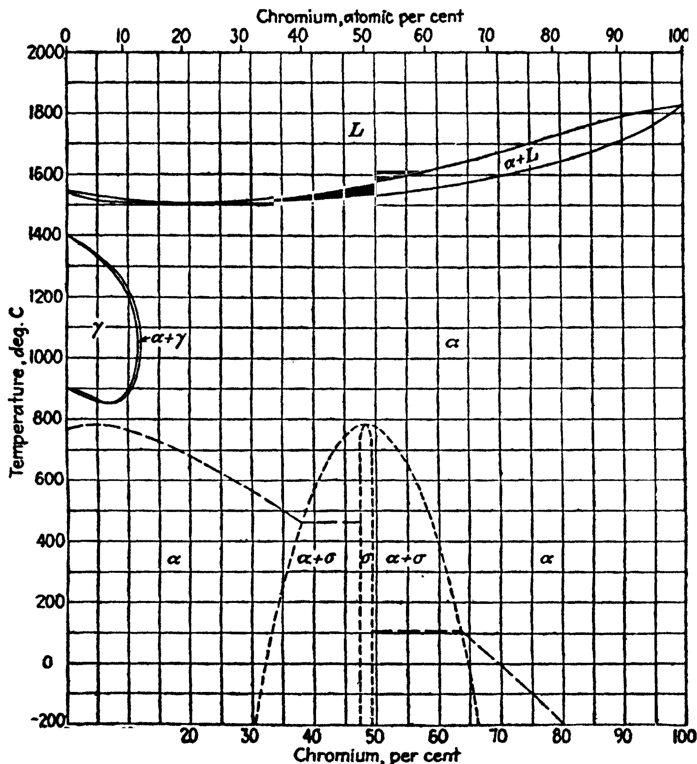


FIG. 76.—The iron-chromium phase diagram. (*From Kinzel and Crafts, "Alloys of Iron and Chromium," Vol. II, McGraw-Hill Book Company, Inc.*)

molybdenum, silicon, tantalum, titanium, tin, tungsten, or vanadium).

By reference to the diagram, it is evident that an iron-chromium alloy containing 10 per cent of chromium in the form of alpha solid solution at room temperature, if very slowly heated, will change to gamma solid solution at 900°C. (1650°F.), and then to alpha solid solution at 1200°C. (2350°F.). A 15 per cent chromium alloy lies

outside the gamma loop and would remain alpha solid solution at all temperatures up to the melting point, *i.e.*, no phase changes occur on heating or cooling. If carbon is added to these iron-chromium alloys, the limit of the gamma loop is moved to higher chromium concentrations; whereas the limit of the loop extends to 12 per cent chromium with negligible carbon, it extends to 18 per cent chromium when the carbon is raised to 0.40 per cent. Furthermore, the addition of carbon causes an increase in the distance between the inner and outer loop, *i.e.*, the area of the two-phase alpha + gamma region is increased. It also is important to recognize that chromium forms carbides which with iron carbide form mixed carbides, $(Cr, Fe)_7C_3$ and $(Cr, Fe)_4C$, in the commercial high-chromium steels. These carbides, like iron carbide, have considerable solubility in gamma iron but little solubility in alpha iron.

The foregoing facts, added to the knowledge that chromium retards the rate of austenite transformation, provide the basis for discussing the heat-treating characteristics of high-chromium steels. Clearly, if the chromium and carbon contents of a steel are such that it lies outside the gamma loop at all temperatures (for example, 16 per cent of chromium and 0.06 per cent of carbon), the steel will remain ferritic at all temperatures. Such high-chromium steels are relatively soft and ductile and cannot be hardened by heat-treatment. On the other hand, steels of such chromium and carbon contents that they fall within the gamma loop at elevated temperatures will respond to heat-treatment. The cutlery steels, containing 12 to 16 per cent of chromium and 0.20 to 0.60 per cent of carbon serve as examples. When heated to temperatures above about 980°C. (1800°F.), alpha solid solution changes to gamma solid solution and the carbides dissolve to form a high-chromium austenitic phase. Due to the high-chromium content, the critical cooling rate will be so low that these steels can be completely hardened (transformed to martensite) by quenching in oil, or even in air (air hardening). When these steels are cooled slowly, the austenitic phase decomposes into pearlite and excess ferritic phase or excess carbide, depending upon the carbon content. With high chromium the eutectoid composition is found to be at much lower carbon contents than in the plain-carbon steels. Thus, with 12 to 14 per cent of chromium an entirely pearlitic structure is obtained at very low rates of cooling when the carbon content is 0.30 to 0.40 per cent, whereas the eutectoid plain-carbon steels contain 0.83 per cent of carbon. The higher carbon, high-chromium steels

are therefore hypereutectoid in type, and may, by proper heat-treatment, be given a microstructure involving excess hard carbide particles which impart the wear resistance desirable in tool and die steels.

The steels containing 20 to 30 per cent of chromium will be ferritic at all temperatures if their carbon contents are less than 0.60 to 0.80 per cent (25 per cent chromium steel is ferritic at all temperatures if it contains less than 0.70 per cent of carbon), and these steels will not respond to heat-treatment.

Chromium has only a moderate strengthening effect on ferrite. As a consequence, the physical properties of annealed high-chromium low-carbon steels are not greatly superior to those of low-carbon steel. Owing, however, to the inhibitive effect of chromium on the rate of austenite transformation, very desirable physical properties may be developed by heat-treatment of the high-chromium steels which lie within the gamma loop at elevated temperatures. These statements are supported by the data in Table 66.

TABLE 66.—PHYSICAL PROPERTIES OF PLAIN LOW-CARBON AND HIGH-CHROMIUM LOW-CARBON STEELS

Steel		Treatment	Tensile strength, psi	Yield strength, psi	Elongation in 2 in., %	Reduction of area, %	Brinell hardness
% C	% Cr						
0.10	0	Annealed	50,000	38,000	44	..	90
0.10	15.5	Annealed	75,000	42,000	33	..	148
0.10	15.5	Quenched and tempered at					
		205°C. (400°F.)	170,000	160,000	8	18	363
		315°C. (600°F.)	168,000	160,000	10	20	363
		425°C. (800°F.)	166,000	160,000	15	45	363
		540°C. (1000°F.)	160,000	148,000	18	46	363
		650°C. (1200°F.)	90,000	83,000	21	50	200

Constitution and Properties of Iron-chromium-nickel Alloys.—As was mentioned previously, nickel lowers A_3 in iron and decreases the "critical cooling rate." It has little effect on A_4, and therefore as nickel is added to iron the area of the region in which gamma solid solution is stable is increased. Chromium, on the other hand, tends to restrict the gamma solid solution region (Fig. 76). When nickel is added to an iron-chromium alloy, it will enlarge the region

in which gamma solid solution is stable. This will be apparent from an examination of the sections of phase diagrams shown in Fig. 77. The lower left-hand section of the figure shows that in an iron-chromium alloy containing 18 per cent of chromium and low carbon, alpha solid solution is stable at all temperatures up to the melting point. However, if 8 per cent of nickel is added to this alloy, it may all be converted into gamma solid solution if the

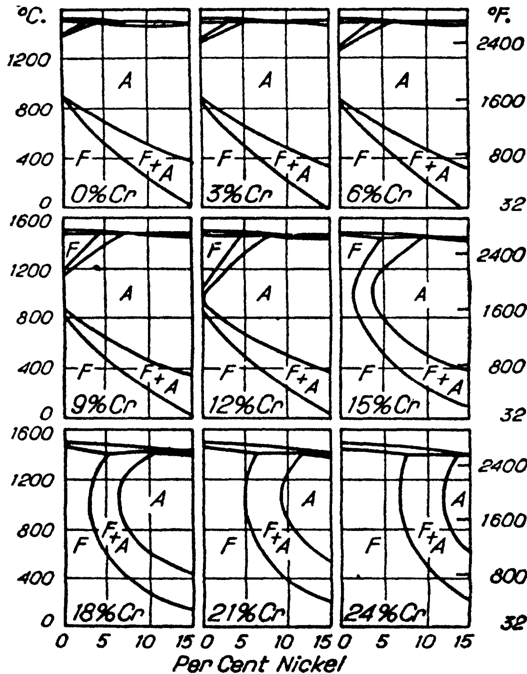


Fig. 77.—The effect of nickel on the constitution of iron-chromium alloys. (*"Metals Handbook,"* 1939 *ed.*, *American Society for Metals*.)

temperature is raised above about 700°C. (1290°F.). By holding for a sufficient time at temperatures above 700°C., low-carbon "18-8" may therefore be converted completely to austenite. If the alloy is then cooled sufficiently slowly, it should begin to transform to alpha solid solution and the transformation should be complete at about 350°C. (660°F.). However, both chromium and nickel strongly depress the rate of phase transformation with the result that only a small amount of alpha solid solution is formed in ordinary slow cooling, and it is easy to cool rapidly enough so that the alloy will be entirely austenitic at room temperature.

Austenitic 18-8, as low as possible in carbon, is about twice as strong as plain carbon steel of the same carbon content, is ductile enough to be readily formed cold into a variety of useful articles, and it may be welded, riveted, and soldered. Owing to its high electrical and thermal resistance, spot welding has been especially useful as a method of fabrication.

Resistance of High-chromium Steels to Corrosion and High-temperature Oxidation.—The resistance of high-chromium steels

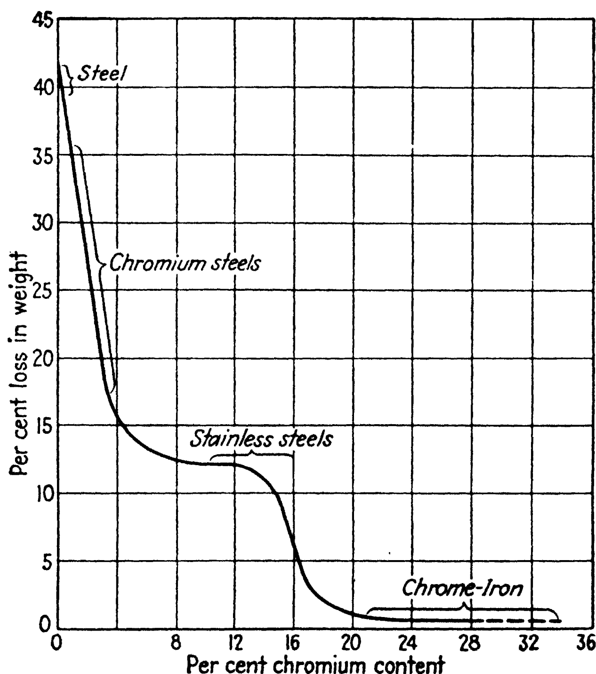


Fig. 78.—The effect of chromium on the resistance of steels to oxidation at 1000°C. (1830°F.). (*From "Book of Stainless Steels," American Society for Metals.*)

to corrosion at ordinary temperatures by the usual aqueous and atmospheric environments, and by many chemicals, is discussed in Chap. IX. The resistance of high-chromium steels to oxidation at elevated temperatures (scaling) accounts for many of their industrial applications. In general, the resistance to high-temperature attack increases with the chromium content in a rather irregular manner as indicated in Fig. 78.

Iron-chromium-nickel alloys, such as 18-8 and alloys still higher in nickel and chromium, a few iron-chromium-aluminum alloys,

and some iron-chromium-nickel alloys containing small percentages of one or more additional elements (tungsten, molybdenum, titanium, copper, or silicon) possess even better resistance to high-temperature attack and to many corrosive environments at ordinary temperatures than the plain high-chromium iron alloys.

The deleterious effect of precipitated iron-chromium carbides, which make high-chromium steels susceptible to intergranular corrosion, the difficulty of producing low-carbon, high-chromium steels, and the advantages gained by stabilizing the carbides by the addition of titanium, molybdenum, or columbium to high-chromium steels are discussed in Chap. IX. Finally, it should be mentioned that the addition of sulfur or selenium to improve the machinability of a high-chromium steel will also make the steel less resistant to corrosive environments.

Creep Resistance of High-alloy Steels.—It long has been known that metals and alloys will deform plastically, or creep, if stressed *even below the yield strength* at sufficiently high temperatures. Indeed, many soft and ductile metals and alloys will deform plastically when stressed at ordinary temperatures; lead, for example, will flow under its own weight. Up until 15 or 20 years ago, the temperatures and pressures involved in power-generating and processing equipment were low enough so that no appreciable plastic deformation occurred when plain-carbon steels and other high-melting alloys were used as materials of construction. In recent years, to gain increased energy efficiencies and to make possible various desirable chemical processes, higher temperatures and pressures have been used in all sorts of industrial equipment from boilers, superheaters, and turbines to petroleum refinery units and synthetic ammonia plants. Turbine failures emphasized the fact that steel, at the temperatures involved, will creep under stresses lower than the values that were considered conservative in good design.

The realization that resistance to creep is a factor of prime importance in the selection of materials of construction and in design has provided the impetus for a great amount of research in this field during the last 15 years. The present state of our knowledge of creep has been summarized by Gillett[1] in his Howe Memorial Lecture. The following statements seem important in considering the engineering aspects of creep:

[1] GILLETT, *Trans. A.I.M.E.*, **135**, 15 (1939). An excellent bibliography is given.

1. A metallic material which is to be used in equipment operating at elevated temperatures under stress should

a. Be resistant to oxidation or other forms of chemical attack by the environment.
b. Have a stable structure that will remain relatively unchanged under the prevailing stress and temperature.
c. Withstand the imposed stress with a harmless amount of distortion for the useful life of the equipment. As one extreme, Gillett mentions turbine disks which should not stretch more than 0.2 per cent in an estimated life of 25 years (200,000 hr.). This means that for this application, the permissible rate of creep is of the order of 1/100,000,000 in. per in. per hr. at the temperatures and stresses involved. In many other applications much larger distortions would not cause failure within the estimated useful life of the equipment.
d. Withstand momentary overloads at the usual operating temperature and fluctuations in temperature for short periods at normal loads.

2. No "short-cut" methods have been successful in evaluating the creep characteristics of materials. All attempts to predict creep characteristics from short-time physical tests at temperature have failed. The only reliable creep data have been obtained by long-time tests that actually measure the amount of creep under applied stress at carefully controlled temperatures. Creep testing requires elaborate equipment and much time and hence is expensive.

3. There is no such thing as a "creep limit" or "limiting creep stress"; *i.e.*, at a fixed temperature for a given material, there is no limiting stress below which creep will not take place.

4. Creep as a function of time under constant stress and at constant temperature may be divided into three stages:

a. The initial stage, which has been called the period of stress distribution and during which there is a relatively large deformation.
b. The second stage in which slip (p. 223) is uniform (constant rate of creep) and much smaller in magnitude than in the initial stage.

c. The final stage in which rate of creep may increase, remain essentially the same, or decrease.

The behavior of a material in the second stage is the most important from the standpoint of engineering applications, but the behavior in this stage cannot be predicted from the behavior in the initial stage. For this reason short-time creep data are of little value.

5. Killed steel has a better creep resistance than rimming steel of the same composition.

6. Among ordinary steels, those of coarse austenite grain size have better creep resistance than comparable steels of fine grain size. However, grain size seems to have little influence upon the creep characteristics of the austenitic high-alloy heat-resisting steels such as 18-8.

7. Carbon and most low-alloy steels containing lamellar pearlite possess better creep resistance than comparable steels in which the carbide is spheroidized.

8. The creep strength of carbon steels can be increased by adding a carbide stabilizer such as molybdenum. Of the low-alloy steels, the molybdenum and the chromium-molybdenum steels probably have the best creep characteristics.

9. Fortunately, the alloy steels that have outstanding resistance to oxidation at elevated temperatures also possess excellent creep strengths at elevated temperatures. As a consequence, 18-8 and steels containing still higher percentages of chromium and nickel, and sometimes one or more additional elements (tungsten, molybdenum, silicon, etc.) in small percentages are finding wide application under high-temperature, high-stress service conditions.

The creep characteristics of a material at any temperature are expressed by stating the creep stress required to produce a certain percentage of elongation in a fixed time; usually pounds per square inch required to produce an elongation of 1 per cent in 10,000 hr., or an elongation of 1 per cent in 100,000 hr. at a specified temperature. Thus, the creep stress required to produce 1 per cent elongation in 10,000 hr. at 650°C. (1200°F.) is 800 psi for killed, plaincarbon steel; 1,800 psi for 0.5 per cent molybdenum steel; 1,800 psi for low-carbon, 15 to 18 per cent chromium steel; and 8,000 psi for 18-8, 25-20, and 20-30 chromium-nickel steels. In general, the high-chromium, high-nickel austenitic steels are more resistant to creep at 820°C. (1510°F.) than are the plain-carbon steels at 650°C. (1200°F.).

Tool and Die Steels

In a study of the historical evolution of our present civilization one might well divide the study into epochs on a basis of the materials used as tools in each historical period: the order would be stone, copper, bronze, iron, steel, and finally high-speed and other alloy steels. We are living in the high-speed tool age. Modern tool steels have an importance to civilization that greatly exceeds their relative tonnage in production. This is evidenced by the fact that the most serious bottleneck in our present (1940–1941) frenzied attempt greatly to expand production in all lines is our shortage of machine and other tools. Parenthetically, one might observe that our present-day efficient machines are not an unmixed blessing because their widespread use has also brought difficult social and economic problems.

Intelligent care in the manufacture, care in the selection and control of heat-treatment, as well as composition, are important in the production of steels of "tool steel quality." Moreover, such steel products as dies for hot or cold forming, ball and roller bearings, races, and valves are made from steels that have the same composition and have been given about the same heat-treatments as tool steels. These products, therefore, must be fashioned from steel of tool steel quality. Many commercial plain-carbon steels have a composition essentially identical with certain plain-carbon tool steels. It is therefore difficult to define the term "tool steel" and there seems little hope of improving upon the classification of tool steels on a basis of composition as given by Gill and reproduced in Table 67. The characteristics of the principal types of tool steel as summarized by Gill are given in Table 68.

The properties that should be possessed by cutting and shearing tools are high hardness, wear resistance, stability of structure at the temperatures attained on the cutting edge of a tool, sufficient toughness to withstand chipping and breakage, and resistance to distortion and cracking in heat-treatment. Forming tools in general must have most of the characteristics of cutting tools and must have resistance to deformation and cracking under sudden temperature changes during use.

Plain High-carbon Tool Steels.—These steels, because of their low cost, are widely used for certain purposes in spite of the fact that they possess low wear resistance, are shallow hardening, have a low resistance to softening at elevated temperatures, and are more susceptible to distortion in quenching compared to the alloy tool

TABLE 67.—CLASSIFICATION OF TOOL STEELS ACCORDING TO CHEMICAL COMPOSITION*

Type no.	Type	Chemical composition, %					
		Carbon	Silicon	Manganese	Tungsten	Chromium	Vanadium
1	High-carbon	0.60–1.40	0.15–0.50	0.10–0.35			
2	Carbon-vanadium	0.60–1.40	0.15–0.50	0.10–0.35	...	...	0.10–0.40
3	Low-chromium	0.60–1.40	0.15–0.50	0.10–0.35	...	...	0.00–0.20
4	Oil-hardening manganese†	0.85–1.00	0.20–0.40	1.00–1.75	0.30– 0.60	0.30– 0.90	0.00–0.25
5	Silicon-manganese‡	0.50–0.70	1.75–2.25	0.70–1.00	...	0.00– 0.40	0.00–0.30
6	Low-tungsten	1.00–1.30	0.20–0.40	0.10–0.30	1.00– 2.50	0.35– 0.60	0.00–0.25
7	Tungsten chisel steel	0.45–0.60	0.20–1.50	...	0.70– 2.50	0.75– 2.00	0.00–0.30
8	Finishing tool steel	1.20–1.40	...	...	3.00– 6.00	0.00– 1.50	
9	Chromium for hot working§	0.70–1.00	...	...	...	3.00– 4.25	
10	Tungsten for hot working	0.25–0.60	...	...	8.00–19.00	1.25– 4.50	0.30–1.20
11	Chromium-tungsten hot working§	0.30–0.50	0.20–1 00	...	0.75– 7.50	1.00– 7.50	
12	High-carbon, high-chromium	1.40–2.45	...	...	...	12.00–18.00	0.00–1.00
13	High-speed	0.55–1.00	...	...	14.00–21.00	4.00– 4.50	1.00–2.25

* From GILL, "Tool Steels," American Society for Metals, Cleveland, Ohio.

† If manganese is 1.50 to 1.75 per cent, it may contain no other alloying elements.

‡ May contain molybdenum.

§ May contain cobalt and/or molybdenum.

steels. In general, high-carbon tool steels must be tempered after quenching at temperatures below 370°C. (700°F.) if hardness is to be retained, and these steels are not satisfactory for service in which the cutting edge of the tool exceeds the above temperature. The principal uses for high-carbon steels of tool steel quality have already been indicated (page 357). Since one cannot obtain marked toughness along with high hardness in plain high-carbon steels, compositions and heat-treatments must be selected that give the best combination of properties for a particular application. The microstructure sought in the heat-treatment of these steels consists of small carbide particles dispersed in a martensitic matrix.

TABLE 68.—CHARACTERISTICS OF PRINCIPAL TYPES OF TOOL STEELS*

Type no.	Usual working hardness, Rockwell C	Resistance to wear	Toughness	Distortion in heat-treatment	Resistance to softening at elevated temperature	Quenching medium	Depth of hardening
1	†	Low	†	High	Low	Water	Shallow
2	†	Low	†	High	Low	Water	Shallow
3	†	Low	†	High	Low	Water	Medium
4	58–62	Low	Medium	Low	Low	Oil	Medium
5	50–57	Medium	Medium	Medium	Medium	Water	Medium
6	62–65	Medium	Medium	Low	Low	Oil	Medium
7	50–55	Medium	High	Low	Medium	Oil	Medium
8	63–66	Medium	Low	High	Medium	Water	Deep
9	45–50	Medium	Medium	Low	Medium	Air or oil	Deep
10	45–55	Medium	Medium	Low	High	Air or oil	Deep
11	43–50	Medium	Medium	Low	High	Air or oil	Deep
12	58–66	High	Low	Low	High	Air or oil	Deep
13	62–66	High	Low	Low	High	Air or oil	Deep

* From GILL, "Tool Steels," American Society for Metals, Cleveland, Ohio.
† Depends upon carbon content and heat-treatment.

Manganese Tool and Die Steels.—Steels of this class (type 4, Table 67), owing to the effect of manganese on the critical cooling rate, can be hardened by oil quenching and thus are less liable to distortion and cracking in heat-treatment. Sometimes these steels are modified by the addition of 0.10 to 0.25 per cent of vanadium to reduce their tendency to grain growth. Other modifications consist in reducing manganese to 1.2 to 1.4 per cent and adding

0.5 per cent of chromium and 0.5 per cent of tungsten, or in reducing manganese to 1.0 per cent and adding 0.75 per cent of chromium. The latter steels are not so susceptible to quench cracking as the higher manganese varieties but they also possess a lower hardness.

Owing to their reasonable price and moderately desirable properties, these steels are widely used as dies for molding plastics, stamping dies, punches, thread-rolling dies, and as master tools and gauges. Because of their wear resistance, toughness, and low cost, the silicomanganese steels, (type 5, Table 67), S.A.E. 9255 and 9260 have been used for punches, chisels, and shear blades. These steels are intermediate between plain carbon and higher manganese steels in hardenability and must be water quenched.

Low-chromium and Low-tungsten Tool and Die Steels.—These steels (types 6 to 9, Table 67) are fair to deep hardening and are not very susceptible to distortion and cracking in heat-treatment. It is possible in general to develop a better combination of hardness and toughness in these steels than is possible with the plain high-carbon tool steels. They are not, however, resistant to tempering and the steels of this group soften when the cutting edge of a tool reaches temperatures in the range 150 to 315°C. (300 to 600°F.). Nevertheless, these steels find important use as taps, reamers, chisels, punches, shear blades, some dies, and cutting tools for smooth finishings at low speeds and feeds.

High-tungsten and High-chromium Tool and Die Steels.—All steels of this group are deep hardening and may be hardened by quenching in oil or air. The steels of type 10 (Table 67) retain their hardness at temperatures as high as 595°C. (1100°F.) and are used for forging dies, shears, and punches for hot-working metals and even as permanent molds for die-casting nonferrous alloys. Steels of type 11 retain their hardness up to working temperatures of about 450°C. (840°F.) and are used as permanent molds for die-casting aluminum alloys and in some instances as forging dies. Steels of type 12 are widely used as die steels because of their high hardness, which is retained up to 480°C. (900°F.), and their superior wear resistance.

High-speed Steel.—The first high-speed steel was developed in America by Taylor and White in 1898. Since that time there has been a slow but steady evolution in the quality and applications of these remarkable tool steels. Their great virtue lies in the fact that they retain their hardness at red heat and permit machining

at high speeds with heavy cuts. Many modern production rates would be impossible without these high-speed tool steels. The composition ranges of the principal types of high-speed steel as summarized by Gill are given in Table 69.

TABLE 69.—COMPOSITION OF HIGH-SPEED STEELS

Type	Composition, %				
	C	W	Cr	V	Mo
18-4-1	0.55–0.75	17.00–19.00	3.50–4.50	0.75–1.25	
20-4-1	0.55–0.75	19.00–21.00	3.75–4.50	0.75–1.25	
14-4-2	0.55–0.75	13.00–15.00	3.50–4.50	1.75–2.25	
18-4-1 Mo	0.65–0.85	17.00–19.00	3.50–4.50	1.75–2.25	0.40–0.90
Molybdenum	0.55–0.75	2.00– 4.00	3.50–4.50	0.75–1.25	6.00–9.00

Equally, if not more, important than composition is the heat-treatment whereby the important properties are developed in these steels. The usual treatment consists in heating the tool slowly to about 815°C. (1500°F.), then rapidly to a little below the melting point. (Incidentally, heating to this temperature would ruin a plain-carbon or low-alloy steel.) With most modern compositions, this top temperature lies in the range 1205 to 1285°C. (2200 to 2350°F.). After holding at the high temperature for a sufficient time, the steel is quenched in oil, or sometimes in air, and then tempered immediately by reheating at 540 to 620°C. (1000 to 1150°F.). Temperatures, time at temperature, rates of heating, and rates of cooling must be carefully determined and controlled to develop the most desirable properties in a steel of given composition. Relatively small departures from a standardized practice may cause undesirable variations in quality and general performance.

Properly treated high-speed steels are hard and strong, but relatively brittle at room temperature. They, in general, retain their hardness at temperatures up to 595 to 650°C. (1100 to 1200°F.). The cutting performance of high-speed steel may be as much as fifty times that of plain high-carbon steel.

The recently developed molybdenum high-speed steels have the advantage of being cheaper and the disadvantage of being harder to heat-treat and more difficult to make and forge. Approximately 85 per cent of the high-speed steel produced is type 18-4-1 (Table 69).

No short-time test has yet been evolved that is satisfactory for evaluating the relative merits of the various brands of tool steels. Relative merit for a particular type of work can best be evaluated by a statistical study of the performance of various brands over a long time.

Cast Irons

Any iron-carbon alloy that contains more than 1.7 per cent of carbon is called a cast iron. Actually, most cast irons of engineering importance contain carbon in the range from 2.0 to 4.0 per cent. Ordinary plain cast irons also will contain 0.05 to 0.20 per cent of sulfur, 0.5 to 3.0 per cent of silicon, 0.50 to 1.0 per cent of manganese, and 0.10 to 1.0 per cent of phosphorus. The solidification of cast iron from the melt has already been discussed (page 316). Since most commercial cast irons contain less than the eutectic carbon concentration (4.3 per cent of carbon), the iron after solidification will consist of primary proeutectic saturated austenite and the eutectic of saturated austenite and cementite (ledeburite). The presence of silicon in iron brings the iron-carbon eutectic to lower carbon concentrations; thus, with 3.0 per cent of silicon, the eutectic carbon concentration is only 3.50 per cent. It is possible, therefore, that the higher-silicon, higher-carbon cast irons will after solidification consist of proeutectic cementite and ledeburite. As solidified cast iron is cooled, more cementite is formed by its precipitation from the austenite solid solution (proeutectoid cementite). When the eutectoid temperature is reached, austenite transforms into pearlite (eutectoid of ferrite and cementite). Silicon is soluble in α iron and will be present in cast iron at ordinary temperatures in solid solution in the ferrite. Phosphorus forms the compound Fe_3P which is slightly soluble in ferrite; however, when phosphorus exceeds 0.1 per cent, Fe_3P forms a eutectic with iron (*steadite*) which is easily recognizable as a microconstituent.

In the foregoing discussion it has been assumed that the cast iron is of such composition and has been treated in such a manner that cementite does not decompose to iron and graphite. Under these circumstances, cast iron at room temperature would be made up of ferrite and cementite. The total cementite would consist of eutectoid cementite in pearlite, proeutectoid cementite precipitated from austenite above the eutectoid temperature, eutectic cementite from the ledeburite, and possibly some proeutectic cementite (if the iron contains more than the eutectic carbon

concentration). It must be remembered, however, that cementite is unstable at all temperatures below the solidification temperatures of iron-carbon alloys and it will therefore, to a greater or less extent, depending upon the composition, rate of cooling, and heat-treatment, decompose into iron and graphite (graphitization). Carbon remaining in the form of cementite is referred to as *combined carbon* and that in the form of graphite is called *free carbon*. Silicon has a

TABLE 70.—TYPICAL ANALYSES OF COMMERCIAL CAST IRONS

Use	Per cent				
	C (total)	Si	Mn	P	S
Auto cylinders	3.25	2.25	0.65	0.15	0.10
Auto pistons	3.35	2.25	0.65	0.15	0.10
Auto castings (general)	3.40	2.60	0.65	0.30	0.10
Auto piston rings	3.50	2.90	0.65	0.50	0.06
Machinery iron:					
Light sections	3.25	2.25	0.50	0.35	0.10
Medium sections	3.25	1.75	0.50	0.35	0.10
Heavy sections	3.25	1.25	0.50	0.35	0.10
Water pipe:					
Light and medium	3.60	1.75	0.50	0.35	0.08
Heavy	3.40	1.40	0.50	0.80	0.08
Plowshares, chilled	3.60	1.25	0.50	0.40	0.10
Plow moldboards	3.75	0.85	0.50	0.40	0.10
High-strength iron, plain	2.75	2.25	0.80	0.10	0.09
Heat-resistant iron, pots, and kettles	3.50	1.15	0.80	0.10	0.07
Caustic pots, plain	3.60	1.00	0.75	0.20	0.07
Ingot molds	3.50	1.00	0.90	0.20	0.07
Car wheel iron	3.35	0.65	0.60	0.35	0.12
Pressure cylinder, air and ammonia	3.25	1.25	0.65	0.20	0.10
Valves and fittings	3.30	2.00	0.50	0.35	0.10

very pronounced effect in promoting graphitization; manganese tends moderately to hold more carbon in the combined form, and sulfur shows a marked effect in opposing graphitization.

The chemical composition of cast iron may be controlled (1) by selection of pig iron, (2) by adjustment of the relative amounts of pig iron, cast-iron scrap, steel scrap, and other additions in the charge of the cupola or air furnace (page 387) and (3) by ladle additions to the molten iron. Unlike the practice in steelmaking, very little effort is made to adjust the composition of cast iron by chemical reactions during the melting process. The recommended

analyses[1] of plain cast irons for some of the most common engineering applications are given in Table 70.

As has been mentioned previously, cast iron cannot be formed into desired shapes by the mechanical processes of forging (hammering or pressing) or rolling at any temperature. It must be formed by casting into molds and, if necessary, machining operations on the solidified material. The processes of melting, molding, and casting are described in Chap. VIII.

Cast iron in which most of the cementite has dissociated into iron and graphite has a gray-black fracture and is therefore known as *gray cast iron*. Iron that contains practically all of the carbon as combined carbon has a silvery white fracture and is called *white cast iron*. In intermediate irons, containing roughly half of the carbon as graphite, the other half being combined, the fracture possesses a mottled appearance, and the name *mottled cast iron* is hence applied. As might be expected, mottled cast iron has properties that are intermediate between those possessed by white cast iron and by gray cast iron.

White Cast Iron.—To produce a white iron, silicon must be low and rates of chill must be high. As carbon is increased, the lower the upper limit for silicon if the carbon is to be retained in the combined form.[2] White irons are very hard and brittle and practically unmachinable. As a consequence, white cast iron has little engineering importance except (1) as an intermediate material in the production of *malleable cast iron* (page 383) and (2) as a thin surface layer produced by rapid chill on the surface of a casting which is composed of the softer, tougher gray cast iron in the interior. The latter are known as *chilled castings* and are widely used as rolls and dies when surface hardness and wear resistance are needed.

Gray Cast Iron.—Roughly 95 per cent of all iron castings are of gray cast iron. Low cost, ease of melting, ease of machining, notch insensitivity, high damping capacity, and high compressive strength are its principal properties, and account for its wide use as an engineering material. The compositions for many of the important uses have been given in Table 70. Gray cast iron is of course much inferior to steel in tensile strength, toughness, and ductility. In spite of these shortcomings which make it unsuitable

[1] "Metals Handbook," 1939 ed., p. 360.

[2] See the Maurer diagram for cast iron in Sisco, "Modern Metallurgy for Engineers," p. 199, Pitman Publishing Corporation, New York (1941).

for many applications, between 5 and 6 million tons of gray iron castings are made in the United States each year.

The structure of a gray cast iron normally consists of a pearlitic steel-like matrix, consisting of ferrite and undecomposed cementite, in which graphite is dispersed. The properties of a cast iron will depend upon the relative amount, composition, and structure of the steely matrix and upon the sizes and shapes of the graphite particles dispersed in the matrix. These matters, and hence the properties of a cast iron, may be controlled by (1) control of composition, (2) control of rate of cooling, and (3) proper heat-treatment after the initial cooling. Graphite particles prevent continuity of the grains of the steel-like matrix and as they increase in size and become more platelike, the strength of the iron decreases and the brittleness increases. The problem of producing high-strength cast iron is therefore one of obtaining a structure that consists of a steel-like matrix containing considerable pearlite with the free carbon (graphite) finely dispersed within this matrix. By application of our improved knowledge of how to attain these desirable structures, it has been possible to produce gray iron castings with tensile strengths of 50,000 psi, whereas 20 years ago the average tensile strength was only 25,000 psi.

Several methods have been used to control the size of graphite particles in gray iron castings: (1) Melt iron of white iron composition and add powdered silicon or calcium silicide as a graphitizer just before the castings are poured. (2) Just before casting, mix a proper amount of gray iron from one cupola with white iron from another cupola. (3) Superheat the molten gray iron to a temperature considerably above the normal casting temperature. (4) Pour a low-silicon iron (which normally would yield a white iron) into a preheated mold. (5) Make proper additions of alloying elements (alloy cast irons). By modern methods it is possible to produce various classes of gray iron castings which possess average properties with the following ranges: tensile strengths, 18,000 to 55,000 psi; compressive strengths, 65,000 to 160,000 psi; shear strengths, 27,000 to 61,000 psi; endurance limits, 8,000 to 25,000 psi; and Brinell hardness numbers, 120 to 270.

Alloy Cast Irons.[1]—The possibility of controlling and improving the mechanical properties of gray cast iron by alloy additions has been mentioned. Chromium, copper, molybdenum, nickel, and possibly a few other elements, alone or in various combinations,

[1] MERICA, *Trans. A.I.M.E.*, **125**, 13 (1937). Howe Memorial Lecture.

have been used for this purpose or also to impart higher wear, corrosion, or heat resistance to the iron.

Nickel (0.15 to 4.00 per cent) promotes graphitization slightly, reduces the size of graphite particles, reduces grain size, strengthens the matrix, and prevents the formation of white iron at corners and edges and in thin sections. Chromium (0.10 to 1.75 per cent) hinders graphitization, reduces the size of graphite particles slightly, and strengthens the matrix. Molybdenum (0.20 to 1.20 per cent) reduces the size of graphite particles and strengthens the matrix. Copper (0.10 to 1.00 per cent) hardens and strengthens the matrix. Titanium or vanadium in small amounts produces a smaller grain size in the matrix and produces small graphite flakes. Alloying additions in the above amounts are chiefly for the improvement of the general physical properties; for imparting the resistance to corrosion and to scaling at elevated temperatures, larger additions are made. For example, an austenitic gray iron containing 14.0 per cent of nickel, 5.5 per cent of copper and 2.0 to 6.0 per cent of chromium has good corrosion resistance and is little attacked by oxidizing atmospheres up to temperatures of 815°C. (1500°F.).

Malleable Cast Iron.—In the production of malleable castings, molten iron of such composition that it will yield a white cast iron on solidification is poured into a sand mold. After solidification and cooling, the hard, brittle casting is malleabilized (annealed) to decompose most of the cementite. When the annealing is accomplished in an oxidizing environment, much of the carbon is eliminated and the final structure consists mostly of ferrite (*white heart castings*). In the United States, the white iron is usually annealed in a nonoxidizing environment provided by packing the casting in a ferrous silicate slag or scale; this treatment yields a *black heart* malleable casting. Although temperatures and holding times during annealing are adapted to the properties desired in the casting, the usual procedure consists in heating up slowly to about 870°C. (1600°F.), holding at temperatures for 40 to 60 hr., and then cooling to room temperature at a rate of about 5°C. (9°F.) per hour.

Malleable cast iron usually contains 2.0 to 2.5 per cent of carbon (practically all in the form of graphite, called temper carbon), 0.7 to 1.2 per cent of silicon, 0.40 to 0.60 per cent of manganese, less than 0.20 per cent of sulfur, and less than 0.10 per cent of phosphorus. The usual microstructure consists of a ferrite matrix in which nodules or "nests" of graphite are dispersed as shown in Fig. 79.

In machinability, malleable castings compare favorably with gray cast iron, and in general physical properties they are comparable to low-carbon steel. They have relatively low wear resistance. Malleable castings are used to the extent of about a million tons per year in the United States in the construction of



FIG. 79.—Malleable cast iron: ferrite (white) and graphite (black); etched, 500 ×. (*Sisco*, "Modern Metallurgy for Engineers," Pitman Publishing Corporation.)

railroad equipment, automobiles and trucks, pipe fittings, agricultural machinery, hardware, and a host of other articles. For some special uses, alloying elements are added to malleable iron to obtain or control certain properties.

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EPSTEIN: "The Alloys of Iron and Carbon," Vol. I, Constitution.
GREGG: "The Alloys of Iron and Molybdenum."
GREGG: "The Alloys of Iron and Tungsten."
GREINER, MARSH, and STOUGHTON: "The Alloys of Iron and Silicon."
KINZEL and CRAFTS: "The Alloys of Iron and Chromium," Vol. I, Low-chromium Alloys.
KINZEL and FRANKS: "The Alloys of Iron and Chromium," Vol. II, High-chromium Alloys.
MARSH: "The Alloys of Iron and Nickel," Vol. I, Special-purpose Alloys.
SISCO: "The Alloys of Iron and Carbon," Vol. II, Properties.

Note on Fig. 72, page 336: The hardenability curves in this figure are for a steel containing 0.74 per cent carbon, 0.41 per cent manganese, and 0.14 per cent silicon. The different curves were obtained by heating the steel at various temperatures to develop different grain sizes and then quenching in brine. The heating temperatures and mean grain sizes (G.S.) corresponding to the various curves were the following: Curve A, 1800°F, G.S.2; Curve B, 1700°F, G.S.3; Curve C, 1575°F, G.S.3.5; Curve D, 1450°F, G.S.4; Curve E, 1375°F, G.S.5. These data are from Bain, *Trans. Am. Soc. for Steel Treating*, **21**, 1106 (1933).

CHAPTER VIII

TECHNOLOGY OF SHAPING METALS AND ALLOYS

By J. C. Warner, Ph.D.

For their various uses, metals and alloys must be provided in the form of articles of definite size and shape, and these are made from molten metal by casting processes, from ingots by the various hot- and cold-working operations, from simple shapes by cutting machining, welding, riveting, soldering, etc., or from metal powders by compression and sintering. It is the purpose of this chapter to give a brief account of the technology of shaping metals and alloys.

Casting Processes

In a broad sense a *casting* is produced whenever molten metal is poured into a container and allowed to solidify. Thus a steel ingot produced by teeming liquid steel into a cast-iron mold is a casting. Usually, however, the term casting is restricted to a solidified metal or alloy whose shape is not to be further modified by hot or cold working. Castings may be made by pouring molten metal or alloy into sand molds, permanent metal molds, or by forcing the molten metal under pressure into a die (die casting). Most iron and steel castings are made in sand molds because of the difficulty of finding a metal mold material that will withstand the high temperatures. Many nonferrous metal and alloy castings also are made in sand molds but the use of permanent metal molds is very common in nonferrous foundry practice.

Melting Metals for Casting.—Metal for gray iron castings usually is produced by melting pig iron and scrap iron in a cupola furnace. The cupola furnace is a vertical, cylindrical, steel structure lined with fire-clay brick and equipped with a door near the top for the introduction of the charge, which consists of alternate layers of coke, limestone, and pig iron and scrap. Air that is not preheated is supplied through tuyères near the bottom. Below the tuyère level the furnace is provided with tap holes and spouts

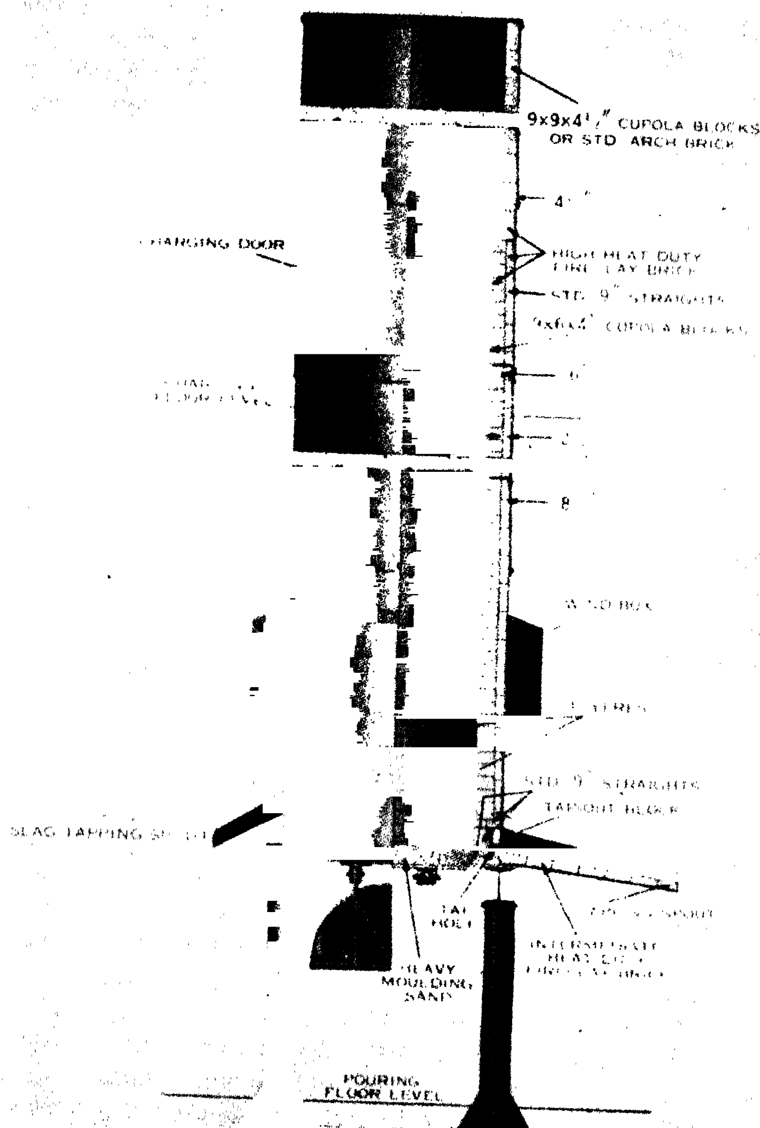


FIG. 80.—The cupola furnace. (*From "Modern Refractory Practice," The Harbison-Walker Refractories Company.*)

for withdrawing slag and molten iron. The construction of the cupola is well illustrated in Fig. 80.

The gases rising through the stack in the cupola are slightly oxidizing in character, resulting in the oxidation of some silicon, manganese, iron, etc., from the charge. The cupola is an efficient type of furnace for iron melting but does not permit the control or modification of metal composition which can be accomplished in the "air furnace." The air furnace is a reverberating-type furnace[1] fired by coal, powdered coal, or oil. It is much used for the production of metal for malleable and alloy iron castings. Electric furnace melting also is being used in the production of high-grade malleable and alloy iron castings.

Melting for steel castings is accomplished in small bessemer converters, open-hearth furnaces, or electric arc or induction furnaces.

Nonferrous alloys usually are melted for casting without much attempt to change composition except by alloying additions. Owing to their higher price more care is used in melting these alloys to preserve quality and to keep melting losses to a minimum. In nonferrous foundry practice, melting furnaces[2] may be divided into (1) those in which the metal is melted in contact with the products of combustion (air reverberatory furnaces and small oil- or gas-fired open-hearth furnaces), and (2) those in which the metal is protected to at least a considerable extent from products of combustion (crucible and electric furnaces). The crucible furnaces may be coke-fired pit furnaces, coke- or oil-fired tilting furnaces, or electric resistance, arc or induction furnaces. Although refractory crucibles of graphite and clay are used in melting most nonferrous metals and alloys, iron pots are satisfactory for many of the low-melting materials.

Molding of Sand Castings.—As the first step in the production of a sand casting, a *pattern* is made. A pattern is a wood or metal copy of the desired article with slightly larger dimensions to allow for the natural contraction that occurs when metals and alloys solidify and cool. The contraction allowance for ordinary gray cast iron is about 1/8 in. per ft.; for white cast iron and steel, 1/4 in. per ft.; for copper and brass, about 3/16 in. per ft.; and for lead and zinc, about 5/16 in. per ft. Molding for small articles may be

[1] "Metals Handbook," 1939 ed., p. 642.

[2] LAING and ROLFE, "Non-ferrous Foundry Practice," Chapman & Hall, Ltd., London (1941).

accelerated by using single or multiple *gated* patterns, consisting of two or more patterns of the article and patterns for the necessary connecting channels or *runners* to permit proper flow and distribution of the molten metal.

For most castings the pattern is divided into two parts and the mold consequently consists of a lower part called the *drag* and an upper part called the *cope.* In making up the drag, the lower portion of the pattern is placed bottom side up on a moldboard; it is surrounded by a rectangular frame of wood or metal, called a *flask,* the space between the pattern and the flask is rammed full of molding sand moistened with sufficient water to render it coher-

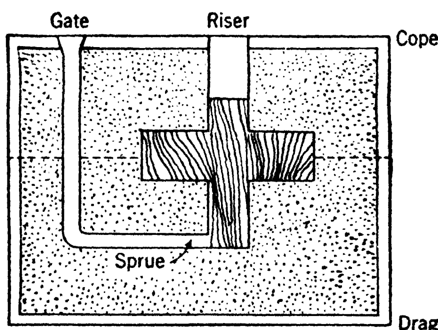


FIG. 81.—Sand mold with pattern, core, etc. (*Reprinted by permission from Joseph Newton, "Introduction to Metallurgy," John Wiley & Sons, Inc.*)

ent, and a number of small vent holes are punched through the sand to the pattern. Next a bottom board is placed over the drag, which is then inverted. *Parting sand* is sifted over the top of the drag, the pattern being kept clean. The cope is made up in a similar manner, additional patterns being used to provide for *gates, runners,* and *risers* (see Fig. 81). Next the patterns are withdrawn, any loose sand is removed from the mold, any portion of the mold surface damaged in the removal of the pattern is repaired, and a facing applied to the mold surface to make it smoother and less easily penetrated by metal.

Hollow castings are made by inserting *cores* which are held in the proper position in the mold by projecting fins which rest in core prints made in the mold by corresponding projections on the patterns or by thin shapes of steel called *chaplets.* After the mold has been prepared as indicated and the cores have been properly located, the cope is locked in place over the drag. In *green-sand molding,* the mold is now ready to receive the molten metal. How-

ever, if the casting is to be made in a *dry-sand mold*, the mold is next dried at 300 to 400°F. After baking, the mold surface is usually coated with a wet mixture of graphite or charcoal with clay. Dry-sand molds are strong, will withstand hard usage, and, if properly vented to permit the escape of gases, will produce smooth, sound castings. They are well adapted to the production of large, heavy castings. In general, castings made in dry sand molds are more sound, smoother, and freer from inclusions of sand and dirt than castings made in green-sand molds.

Runners, gates, and risers have been mentioned. The runner is the canal through which the molten metal is poured. It has an enlarged basin at the top and is connected to the mold at the bottom by an opening called a gate. Risers are vertical canals leading from the high points in the mold to the top of the cope. They serve to vent the mold, to supply metal as the casting solidifies, and to carry off dirt and inclusions from the casting.

It frequently is desirable to accelerate the rate of cooling of certain parts of a casting, either to make the cooling rate of heavy sections of a casting more nearly equal to the rate for thin sections, or to harden the surface of a casting which is to be subjected to heavy wear. This is accomplished by inserting pieces of cast iron or other suitable metals called *chills*, so that they form a portion of the mold surface and extend back from the surface. Owing to the higher heat conductivity of the chills, heat is transferred from the casting to the surroundings more rapidly at these points. Sticking of the casting to the chills is prevented by coating the exposed faces of the latter with shellac and graphite or with a light oil. The bearing surfaces of rolls and the treads of car wheels are cast against chills.

Loam molds frequently are used for large iron castings which are bounded by a surface of revolution. Flywheels are generally cast in loam molds. For such molds an outer casing is built of brick or iron lined with brick. This casing is plastered with a moistened loam mixture and the surface of the mold is generated by revolving a sweep designed to conform with the surface desired in the casting. After baking and facing, the mold is ready to receive the molten metal.

Molding sands when made up in the form of a mold must be sufficiently refractory and strong to withstand handling and the pressure and strain produced by the molten metal. In addition they must be sufficiently porous to permit the escape of air, of steam

from moisture in the sand, and of gases generated during solidification of the casting. The sands in common use in both iron and nonferrous foundry practice are either natural or synthetic mixtures consisting principally of free silica and clay, but usually containing small amounts of magnesia, lime, titania, iron oxides, and alkali metal oxides. Free silica will range from 55 to 85 per cent and clay from 12 to 30 per cent. The clay serves as a binder for the silica grains, imparting strength to the mold. However, the higher the silica content, the more refractory is the mold. Hence the clay content is kept to a minimum in making castings of high-melting-point metals and alloys such as steel castings. In general, physical tests are more nearly indicative of the suitability of a molding sand than exact chemical analysis. For this reason standard tests[1] have been devised for fineness, particle size and shape distribution, permeability, crushing strength of standard rammed specimens, cohesiveness, strength in shear, moisture content, etc.

Loam sand is a highly bonded molding sand which may contain as much as 40 per cent of clay and usually contains more or less decayed organic matter. The term also is used for synthetic mixtures made of clay and sand with some sawdust or similar material as an addition.

Core sands resemble, as a rule, the medium- or coarse-grained molding sands of low-clay content. Cores in general must be more refractory and permeable than the mold. They must be strong enough to withstand the pressure of the molten metal but must permit ready escape of gases and contraction of the casting as it cools and solidifies. For small cores, sand with no clay frequently is used, the necessary bond being obtained by the use of adhesives or *core binders* such as molasses, starch, dextrin, resins, pitches, tars, and oils. The most important oil binder is linseed, although tung, soybean, cottonseed, corn, fish, and rosin oils also are used. Cores also are strengthened by the use of reinforcing wires.

Parting sand used between the cope and the drag is a highly refractory fine silica or burned sand containing no binder. It cannot be rendered cohesive by the addition of water and prevents the lower surface of the cope from adhering to the upper surface of the drag. Soot from a smoky flame, lycopodium powder, and various artificially prepared products have been successfully used as parting materials.

[1] Standard tests are published by the American Foundrymen's Association, Chicago, Ill.

Facing materials are used to line the mold to prevent the formation of a scale by a reaction between the silica of the sand and the metal oxide developed at the surface of the molten metal. Thus facing materials assist in the production of castings that leave the mold freely with a bright surface and can be cleaned at low cost. Fine soft coal, graphite, charcoal, and talc are among the substances that are mixed with six to fifteen times as much fine molding sand to make facings.

The production of castings from ferrous and nonferrous metals is an intricate art which only recently has begun to benefit from scientific research. It is beyond the scope of this book to describe the art in detail. It is our purpose here to give engineers a brief account of the process so that they may be in better position to understand its limitations and to use judgment in the design of cast articles. The following points should be kept in mind in the design of castings: (1) Patterns should be of such shape that they may be removed without damaging the mold. For intricate shapes it is necessary to make the pattern in several parts. (2) Fillets of large radius should be provided at all sharp angles and corners to avoid planes of weakness. (3) Avoid joining light and heavy sections whenever possible to prevent high stresses at their junction due to unequal rates of cooling. If such junctions are unavoidable, the heavy sections should be provided with *chills* to ensure more nearly equal rates of cooling. (4) Avoid designs in which certain parts of the casting would be held rigidly by the mold leading to high contraction stresses.

For more detailed discussions of the production of castings in sand molds, the reader should consult the references given at the end of this chapter.

Permanent Mold Castings.—When a large number of identical metallic objects are to be produced by casting, it is advantageous to carry out the operation in permanent metal molds which can be used over and over again, thus eliminating the work of rebuilding or extensively repairing sand molds for each casting. Owing to the high temperatures involved it is difficult to find a permanent mold material for iron and steel castings unless the casting is of a simple shape such as an ingot. Many of the nonferrous alloys are satisfactorily cast in permanent metal molds to produce sounder, cleaner castings with better mechanical properties than can be obtained by casting in sand molds. Among the alloys that are especially suitable for permanent mold casting are lead-antimony-

tin *printing* or *type* metals, aluminum bronzes, aluminum-silicon alloys, and various alloys of magnesium, copper, and zinc.

Most permanent metal molds consist of two cast-iron halves with the parting surface arranged vertically. Hence most permanent mold or *chill* castings are produced with the largest dimension parallel to the vertical parting plane. Openings in permanent mold castings are produced by the use of steel or sand cores. In some cases slightly tapered steel cores pass through the mold wall and can be pulled independently of the operation of the mold. Since, as in sand casting, the molten metal flows into the permanent mold under the force of gravity, the mold must be vented to permit the escape of gases and must be provided with risers to feed metal to the casting during solidification. Owing to their higher thermal conductivity, castings solidify and cool at a much more rapid rate in metal than in sand molds.

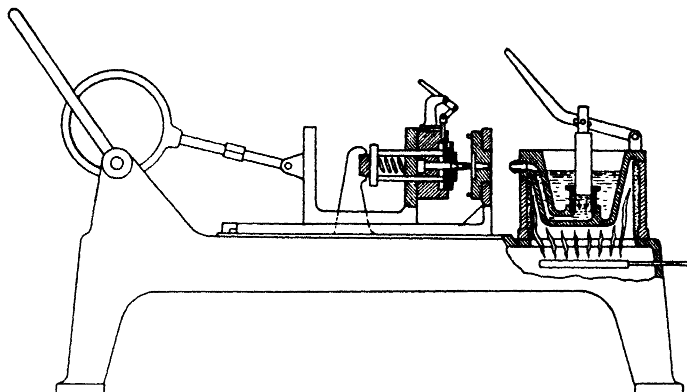


FIG. 82.—Plunger-type die-casting machine. (*From Sachs and Van Horn, "Practical Metallurgy," American Society for Metals.*)

Die Casting.—In the die-casting process, molten metal is forced under pressure through a gate into a die. The gate usually is perpendicular to the parting surface of the die. Dies for tin and lead alloy castings (page 256) can be made of plain-carbon steel but special chromium-vanadium and chromium-tungsten-cobalt steels (page 375) are generally used in dies for casting aluminum (page 240) and zinc (page 257) alloys. The pressure for forcing metal into the die may be generated by the forward motion of a piston in a cylinder filled with molten metal or by admitting air at pressures of 200 to 500 psi behind metal in a gooseneck attached

to the die. A commonly used plunger type of die-casting machine is illustrated in Fig. 82. The cylinder in which the plunger operates is submerged under molten metal in a pot and fills with metal through a side port on the upstroke of the plunger.

Dies usually are water cooled and should be provided with vents on the parting surface to permit the exit of air. The casting normally adheres to that side of the die in which the larger part of the casting is formed. This side is therefore provided with devices for ejecting the casting. With alloys of suitable composition, it is possible to produce smooth, clean die castings which require little finishing and are sounder than castings produced by other methods. It should be noted that the linotype and monotype machines used in the printing industry are specialized die-casting machines.

The die-casting process has found a continuously expanding field of application[1] for the mass production of a great variety of castings due to the high speed of the process and the low cost of finishing operations.

Centrifugal Castings.—This process is limited to the production of relatively simple shapes which have rotational or nearly rotational symmetry. Its main field of application has been in the production of large-size tubing or pipe of cast iron, steel, bronze, gun metal, nickel, Monel, aluminum, lead, etc. Interesting applications are found in the production of centrifugally cast steel gun barrels and in the lining of cylindrical or semicylindrical bearing shells with Babbitt and cadmium base alloys. The most complicated shapes yet made by centrifugal casting probably are steel and bronze gears.

The centrifugal casting machine consists of a refractory or metal cylindrical mold which is rotated at speeds up to 10,000 r.p.m. for castings of small diameter. Pouring spouts are provided at one or both ends of the mold, and the metal supply is carefully controlled. The pressure on the metal is greater than in sand casting due to the centrifugal force generated by the rotational motion. This results in a greater density, a finer grain structure, and better mechanical properties than are obtained in ordinary castings. The metal nearest to the rotational axis has the same function as the metal in the gates and risers in ordinary castings. This rather porous layer, relatively high in inclusions and impurities, frequently is machined from the inner surface of the casting.

[1] For information on the principal die-casting alloys, see "Metals Handbook," 1939 ed., pp. 1302, 1594, 1733, 1770.

Defects in Castings.—A metal or alloy is said to have excellent casting properties if it will completely fill a mold of intricate design to produce a sound casting possessing quite uniform mechanical properties. It is safe to say that a completely sound casting has not yet been produced in practice, but successful foundry practice requires that imperfections in castings be held to a minimum. The principal defects are the following: rounded-off edges, *cold shuts*, and *misruns* due to the fact that the metal was too cold to completely unite and fill the mold before solidification. An alloy with which these difficulties are not usually encountered is said to have good mold-filling capacity, high *fluidity*, or good *running quality*. Cracks in castings are a common defect, and two types are recognized. *Cooling cracks* are characteristic of brittle alloys such as cast iron. A casting may be perfect after complete solidification but, during cooling, stresses may develop due to unequal rates of cooling or to restraints imposed by the mold which exceed the strength of the material, and a crack will develop during cooling, afterward during machining, or in a service involving vibrations. A second type of crack, called a *shrinkage crack*, is more common in nonferrous alloys. It is believed that these cracks develop at a high temperature where certain localized regions, such as grain boundaries, still remain liquid, and very little force is needed to cause rupture. Alloys susceptible to shrinkage cracking are said to be *hot short*.

Cavities of various sorts in solidified castings represent an important type of defect. *Shrinkage cavities* are analogous to *pipe* in an ingot. These cavities should form outside the casting proper, in the gates and headers, if the mold is properly designed. Large *blowholes* may result either from entrapped air due to improper venting and feeding or from gas produced in reactions between the molten metal and moisture in the sand. Small *pinholes* usually are caused by the entrapment of gases that are dissolved in the liquid metal and come out of solution during solidification. In addition small intercrystalline fissures of rather obscure origin have been observed.

Internal defects in castings are revealed by X-ray inspection if sections are not too thick (up to about 5.5 in. for steel). Defects in heavier sections may be detected by use of radiographic methods. The *magnaflux* methods reveal surface or near-surface cracks in steel. In this method the surface is covered with a suspension of very fine iron or magnetite powder, after or during magnetization.

Cracks are revealed by local accumulations of the magnetic powder.

Shaping by Hot or Cold Working

The major portions of metals and alloys are formed into the desired shapes by progressive plastic deformation of the solid

Method	Principle of operation	Action on metal
Forging Hammering Pressing		Pressure on unconfined metal
Die forging		Forces metal into a die
Extrusion		Squirts metal through a die
Piercing		Pressure exerted by mandrel on confined metal
Wire drawing		Wire or rod drawn through die
Tube drawing	(a) (b)	(a) Reduction in wall thickness between die and plug (b) "Sinking" or reduction in diameter

Fig. 83.—Shaping operations. (*From Liddell and Doan, "Principles of Metallurgy."*)

metallic material. These operations begin with the metal or alloy in the form of an ingot. The temperatures employed vary all the way from temperatures slightly under the melting point to room

temperature, being adjusted to the character of the metal and the type of the operation.

Inasmuch as these operations are essentially mechanical in nature, a detailed discussion is beyond the scope of this book. The

Method	Principle of operation	Action on metal
Stamping		(a) Curving plates (b) Curving ends of cylinder
Cupping Flanging Spinning		Bending edges of disk
Deep drawing		Stretching of walls (cartridge manufacture, automobile bodies)
Rolling of sheets, beams, and rails		Stretching by rolling
Piercing (Mannesmann)		Rolls and mandrel rotate in same direction

FIG. 83.—Shaping operations (continued).

principle of operation of each of the common hot- or cold-working methods is well illustrated in Fig. 83.

Shaping by Cutting and Joining

Frequently the dimensions given to metallic articles by the processes of casting, hot working, or cold working, are not sufficiently precise to meet requirements and the needed precision in dimensions is obtained by such operations as machining with lathe tools, sawing or flame cutting, drilling, milling, and grinding. Furthermore, many articles of intricate design are made by the

various machining operations, starting with solid metal or alloy in the form of such simple shapes as bars, rods, wires, sheets, plates, and pipes. The production of screws and bolts from rod serves as an example. Finally, everyone is familiar with the fabrication of more intricate shapes by joining suitable simple shapes by the processes of riveting, bolting, soldering, brazing, and welding.

Machinability.—For any metal or alloy that is to be subjected to machining operations, the machinability[1] is an important property. The greater the machinability, the more satisfactory the operation from the standpoint of cost, speed, and character of the finish on the article. The relation between composition and structure and machinability is not well understood, and most of our present knowledge has been obtained empirically. The wide interest in the free-machining sulfur- and lead-bearing steels is evidence of the importance of this subject in industry. As has been indicated, the factors of importance in machinability are cutting speed, tool life, power consumption, the finish left on the cut surface, and the accuracy of dimensions of the finished product. Standard tests have been devised to measure one or more of the above factors.

Flame and Arc Cutting and Machining.—Flame cutting[2] has become an important operation for contour cutting of machine and structural parts from plate stock. A cutting torch, hand or mechanically guided, burning acetylene, propane, or other fuel gases in oxygen, serves to raise the metal to its kindling temperature (about 1500° F. for steel). Another jet on the torch supplies oxygen at high pressure to the heated surface and supports the exothermic combustion reaction. The oxygen jet also removes some molten metal from the cut without oxidation. Very heavy sections may readily be cut with the torch and close dimensional tolerance can be maintained if the torch is mechanically guided. Owing to the high thermal conductivity and heat capacity of the mass of metal adjacent to the cut, the temperature of the cut surface drops at rates comparable to those attained in quenching. The surface hardening thus induced is not troublesome with steels containing less than 0.30 per cent of carbon. Steels with over 0.30 per cent of carbon and some alloy steels harden to such an extent that the cut surface will have poor machinability and will be susceptible to cracking and warping. For these steels this difficulty may be overcome by flame annealing or tempering following the

[1] "Metals Handbook," 1939 ed., pp. 634, 839, 891, 1318, 1940, 1603, 1679.
[2] "Metals Handbook," 1939 ed., pp. 921–939.

cutting operation. With proper equipment and precautions it is even possible to flame-cut metals submerged under water.

Electric-arc cutting also has found some applications. In the process the metal is melted away due to the heat generated in the arc. It does not equal flame cutting from the standpoint of smoothness, quality, or accuracy of the cut surface.

Welding, Soldering, and Brazing.[1]—In these processes, metals, after being joined, are held together by forces of interatomic attraction. It is essential, therefore, that the surfaces to be joined be made clean, either by cleaning previous to joining or by fluxing off scale and other impurities during the operation.

Pressure welding is accomplished by heating the parts to be joined into the plastic range and then applying pressure sufficient to give intimate contact and to squeeze out any scale, dirt, etc., that would interfere with the union. The hammered welds of the blacksmith were of this type. Today most pressure welds are made by heating the parts electrically. Current flowing through the parts to be joined heats them most rapidly at the contact between the parts where the resistance is the highest. When the parts are plastic, pressure is applied to squeeze out oxide and slag and form the union. This method is applied to both *butt* and *lap welding* in the production of pipe out of sheet by rolling the sheet into a cylinder and welding the longitudinal seam. It has many other applications in the fabrication of automobile bodies, metal furniture, refrigerators, etc. When electrical power is applied in large amounts for short periods, special names have been given to various modifications of the process: *flash welding, spot welding, percussion welding, projection welding, shot welding,* etc. It is an interesting fact that about 3,500 spot welds were made in fabricating the body and chassis of a recent model of the Ford V8.

Fusion welding includes those joining processes in which the intimate union between the parts is obtained by actual fusion of metal along the contact. In fusion welding, the connecting metal, whether melted from the edges to be joined (autogenous welding), or supplied separately by using welding rod, solidifies from the liquid state and usually cools below the recrystallization temperature without any applied load sufficient to cause deformation. A fusion weld is therefore essentially a chilled casting. In some cases,

[1] "Metals Handbook," 1939 ed., pp. 220–256, 1205–1215. HEYER, "Engineering Physical Metallurgy," pp. 387–412, D. Van Nostrand Company, Inc., New York (1939).

subsequent operations such as hammering and annealing are employed to modify the cast structure of the weld beneficially. On the other hand, the hammering or compression in pressure welding brings about a certain amount of grain refinement, recrystallization, and grain growth and makes the union essentially a forging. The heat necessary for fusion welding may be supplied by the oxyacetlyene flame, by an electric arc between metallic or between carbon electrodes, by the atomic hydrogen torch,[1] or by very exothermic chemical reactions as in the thermit[1] process.

Many important metallurgical problems have arisen in the various welding processes. Most of these are due to the fact that metal in the weld usually is of slightly different composition than the remainder of the metal, and to the very great differences in temperatures and rates of heating and cooling at the weld and in the adjacent metal. Important scientific and engineering investigations of these problems have been made in recent years, but the reader must consult the references for this information.

In *soldering* and *brazing*,[2] the parts to be joined are heated but not melted, and a lower melting alloy, which will adhere to both surfaces after solidification, is fused over the union. There is no sharp distinction between soldering and brazing; when the joining is accomplished by the use of low-melting-point alloys it is called soldering; the term brazing is applied when the alloys have high melting points. The compositions of the various soldering and brazing alloys and their utilization are discussed on pages 251 to 256.

Powder Metallurgy

Powder metallurgy[3] is the art of making objects by the heat-treatment of compressed metallic powders. The process may be applied to a single metal powder, to mixtures of metal powders, or to mixtures of metals and nonmetals. The pressing operation may be carried out at ordinary or at elevated temperatures depending upon the composition and the properties desired in the product. In a sense, powder metallurgy is an old art. Wollaston, in 1828,

[1] "Metals Handbook," 1939 ed., p. 225.

[2] "Metals Handbook," 1939 ed., pp. 1205–1215. For an excellent summary of solders and their properties see Rhines and Anderson, *Metals & Alloys*, **14**, 704 (1941).

[3] "Metals Handbook," 1939 ed., pp. 104–105. Claus, *Ind. Heating*, **6**, 926, 1032 (1939). Jones, "Powder Metallurgy" Edward Arnold & Co., London (1937).

reported to the Royal Society on the production of dense ductile platinum from platinum powder by the process of compressing and sintering. Ductile tungsten, molybdenum, and tantalum have been made from the respective metal powders by this process for some years. From the standpoint of a process that has wide application in forming objects of definite shape from a great variety of powder compositions, the art is comparatively new.

Applications of Powder Metallurgy.—The present-day applications of powder metallurgy may be classed as follows:

1. The production of dense ductile forms of the high-melting-point metals, such as tungsten, molybdenum, and tantalum from these metals in powder form.

2. The manufacture of porous and graphite-containing metal bearings.

3. The production of cemented hard carbides, tungsten, molybdenum, and tantalum carbides in a matrix of cobalt or nickel, for cutting and wear-resisting tools, and for dies that must withstand unusually severe service.

4. In making electrical contacts consisting of a current- and heat-conducting matrix in which are embedded wear-resisting particles.

5. In the production of heat-treated powder compacts of definite shape which compete with castings and shapes made by the more conventional methods.

In the first four fields, we have applications that are not possible by other methods. In the fifth field, powder metallurgy can compete with the older methods to a limited extent only.

Production of Metal Powders.—At the present time, the following metal, alloy, and nonmetallic powders are available in very pure form and are finding fields of application: aluminum, antimony, bismuth, brasses, bronzes, cadmium, chromium, cobalt, columbium, copper, gold, graphite, iron, lead, manganese, molybdenum, nickel, palladium, silicon, silver, tantalum, tellurium, tin, titanium, tungsten, vanadium, and zinc. Furthermore, many metal phosphides are available as powders, and some powders consisting of one metal coated with a thin film of another metal have been used.

The various metals are produced in powdered form by one or more of the following methods:

1. Deposition from a gas. Typical of powders by this method are iron and nickel produced by the decomposition of the gaseous metal carbonyls.

2. Electrolytic processes. There are three distinctly different electrolytic methods: (*a*) A hard brittle electrodeposit is obtained which is subsequently ground to a powder. (*b*) The powder is deposited directly as such. (*c*) A soft spongy deposit is obtained, which may be rubbed into a powder.

3. Chemical reduction of the finely divided oxide or other compound of the metal by hydrogen or other reducing gases at the lowest temperature at which the reduction can successfully be accomplished. This method is very similar to that used in the production of many metal catalysts.

4. Mechanical methods: pulverizing, grinding, and stamping.

5. Other methods that are of limited use are (*a*) atomization of molten metal; (*b*) precipitation of metal in finely divided form by reducing a compound of the metal in solution; (*c*) controlled condensation of metal vapors obtained by direct distillation; and (*d*) condensation of metal vapors produced in the electric arc or other types of electric discharge in controlled atmospheres.

Most metal powders are produced by the first three methods. The following properties of powders are important in determining their behavior in the powder metallurgy process: particle size, particle size distribution, shape (sphere, plates, etc.), purity, oxide content, apparent density, cohesive ability, and flow characteristics.

Mixing, Compression, and Heat-treatment.—Mixing in tumblers or ball mills precedes the compression operation if two or more metal powders are to be blended or if various lots of powder of a single metal are to be mixed to obtain a desirable particle size distribution. The powders are then pressed in dies, usually at room temperature but sometimes at elevated temperatures, using hydraulic, cam, friction, or knuckle-type presses that develop pressures in the range from 5 to 100 tons per square inch. The compression ratios vary from 3:1 to as high as 8:1 depending upon the character of the powder and the article being made.

The compressed compact is next given a suitable heat-treatment. This treatment usually is accomplished in furnaces with controlled atmospheres or in vacuum. During this operation gases may be absorbed or eliminated, oxide impurities may be reduced, diffusion of one metal into another and crystal growth may occur. The porosity of objects made by powder metallurgy may be estimated by comparing the density with that of highly worked material of the same composition. For most purposes it is desirable to reduce the porosity to a minimum. In the production of oilless bearings,

however, porosity is desirable and is intentionally created in the heat-treated articles by the incorporation of volatile salts or metals which evaporate at the temperatures employed to leave a more or less interlocking network of pores.

For many applications, the compressed and heat-treated product will possess sufficiently precise dimensions. If greater accuracy of dimension is required, the heat-treated object is subjected to a machining or coining operation.

For further information on the technology of shaping metals and alloys, the reader should consult the references given throughout and at the end of this chapter.

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CHAPTER IX

CORROSION OF METALS AND ALLOYS

By J. C. Warner, Ph.D.

Most common metals and their alloys are attacked by ordinary environments such as the atmosphere, water, or aqueous solutions, to form compounds of the metal. This destruction of metals and alloys by chemical attack is known as *corrosion,* in contrast to *erosion* which means destruction by mechanical agencies. The chemical attack of an environment upon a metal results in the oxidation of the metal and the formation of a corrosion product, usually the oxide, hydrated oxide, hydroxide, carbonate, sulfide, etc. In most cases the corrosion product is insoluble in the environment and forms a separate phase on or adjacent to the metal. The corrosion of a metal is essentially the reverse of the process whereby the metal was obtained from its ore. In obtaining a metal from its ore by smelting, electrowinning, etc., energy must be supplied to the process; in the reverse process, corrosion, energy is liberated.

The economic importance of this subject is emphasized by the estimate that the annual loss to the world through the corrosion of metals is approximately 2 or 2½ billion dollars. For this reason, research and development work leading to a better understanding of the corrosion process and means for its prevention are of more than usual interest and importance.

In any discussion of corrosion and its prevention it is important to recognize that both the extent and rate of attack will depend upon the nature of the environment as well as upon the nature of the metal or alloy. The importance of the environment is neglected too frequently. Progress has been made on the corrosion problem along several definite lines:

1. The development of alloy compositions which are less liable to attack in certain environments.

2. The adjustment of environments so that materials of otherwise satisfactory properties are less liable to attack.

3. The development of suitable protective coatings. The coatings may be metallic, inorganic, or organic in nature.

4. Cathodic protection.

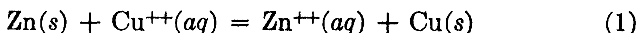
Along each of these lines, progress has been accelerated by improvements in our understanding of the fundamental theory of the mechanism of the corrosion process.

It is generally agreed that metals may be corroded by direct chemical attack or by an electrochemical mechanism. Reactions of dry chlorine, hydrogen sulfide, oxygen, and other dry gases with dry metals are examples of direct chemical attack. The scaling of iron or steel in soaking pits, reheating furnaces, and during hot working, undoubtedly is an example of direct chemical attack. On the other hand, it now seems well established that in most cases the attack on metals and alloys by moist air, water, or aqueous solutions proceeds by an electrochemical mechanism.

The Electrochemical Mechanism.—When a metal corrodes, it is oxidized (its valence is increased by the loss of electrons) and some substance in the environment is reduced (its valence is decreased by the gain of electrons). To say that corrosion occurs by an electrochemical mechanism means that these two parts of the process do not take place at the same spot on the metal surface but on different, usually not widely separated, areas. The area over which metal is attacked is called the anode and that at which some substance from the environment is reduced is the cathode. If the process is to continue, an electrical current must flow between these areas through the environment (usually an aqueous solution) and between these areas in the metal. The combination of anode areas, cathode areas, and aqueous solution constitutes a small galvanic cell and the corrosion reaction proceeds with a flow of current in a manner analagous to the way current is generated by chemical action in a primary cell or in a storage battery on discharge. To understand corrosion by the electrochemical mechanism it is necessary to have some knowledge of the principles and phenomena related to galvanic cells in general.

Galvanic Cells.—Reactions that proceed with the liberation of energy are called spontaneous reactions because they can proceed of their own accord without the application of energy from an outside source. Oxidation-reduction reactions are reactions in which electrons are transferred from the substance being oxidized to the substance being reduced. Spontaneous oxidation-reduction reactions are therefore reactions in which a liberation of energy accom-

panies the electron exchange. The displacement of cupric ions from solution by metallic zinc is a reaction of this type. The total reaction



$$Zn(s) + Cu^{++}(aq) = Zn^{++}(aq) + Cu(s) \quad (1)$$

may be divided into the two parts



$$Zn(s) = Zn^{++}(aq) + 2e \text{ [oxidation of Zn(s)]} \quad (2)$$



$$Cu^{++}(aq) + 2e = Cu(s) \text{ [reduction of } Cu^{++}] \quad (3)$$

If metallic zinc is dipped into a solution containing zinc ions, and metallic copper in a solution containing cupric ions, the two solutions being separated by a porous diaphragm or by gravity, the reaction does not proceed because the zinc atoms cannot come in

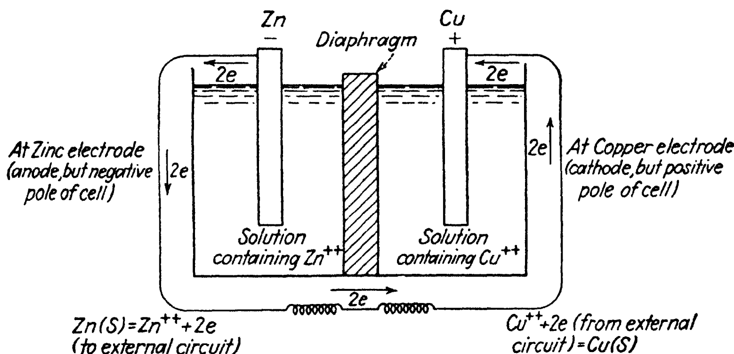


FIG. 84.—The Daniell cell.

direct contact with the cupric ions. If, however, the metallic zinc and copper are connected by means of a conducting wire, the reaction will proceed, the electrons passing from the metallic zinc through the external circuit to the copper where they are given to the cupric ions. This flow of electrons through the external circuit constitutes an electrical current and such a current may be used to do electrical work. This arrangement (Fig. 84) for carrying out the spontaneous displacement of cupric ions by metallic zinc with the production of electrical energy is a primary or galvanic cell (Daniell cell).

If in a galvanic cell, such as the one just described, the electron exchange is allowed to take place only very slowly, one is able to obtain practically all of the energy liberated in the oxidation-reduction reaction as electrical energy in the external circuit.

$$\text{Energy liberated in reaction} = \text{electrical energy produced}$$
$$\text{Electrical energy produced} = \text{volts} \times \text{amperes} \times \text{time}$$

The quantity of electricity (amperes × time) that will flow through the external circuit when gram equivalent weights[1] of oxidizing and reducing substances react in a galvanic cell is fixed by Faraday's law and is equal to 96,500 amp.-sec. (coulombs) or 26.81 amp.-hr. (one Faraday of electricity). Thus for every 32.69 g. of zinc oxidized and every 31.78 g. of cupric ions reduced in the Daniell cell reaction, 96,500 amp.-sec. or 26.81 amp.-hr. of electricity will flow through the external circuit. Since the amount of electricity produced when reaction occurs between gram equivalents of reducing and oxidizing substances is the same in all cells, the differences in the energies liberated in the various cell reactions manifest themselves as differences in cell voltages. If Q represents the energy liberated when gram equivalents react, E represents the cell voltage, and F denotes the Faraday, one may write the following equality when the cell is discharged under such conditions that all of the available energy liberated in the chemical reaction is converted into electrical energy:[2]

$$Q = FE \tag{4}$$

Evidently, then, the cell voltage E is proportional to Q, and a cell in which the reaction liberates a large amount of energy per gram equivalent will have a high voltage. When a cell is discharged under such conditions (extremely low rate of discharge) that all of the available energy from the chemical reaction is converted into electrical energy, the cell is said to be reversible, and E under these conditions is called the reversible electromotive force of the cell. Thus, we may consider E (reversible) as a measure of the *driving*

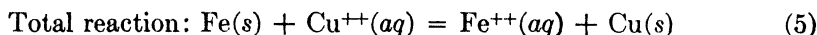
[1] The gram equivalent weight of an element or substance is the atomic or molecular weight divided by the valence change. Thus, in the foregoing example the valence of zinc is increased from 0 to +2 (valence change = 2); hence a gram equivalent weight of zinc = atomic weight of zinc/2 = 65.38/2 = 32.69 g. The valence change for copper in the reaction also is 2 and a gram equivalent weight of copper = 63.57/2 = 31.78 g.

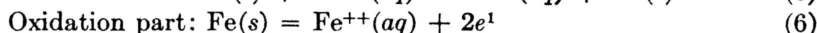
[2] To be accurate, it must be mentioned that Q represents the decrease in the *free energy* or *potential energy* that has occurred in the chemical system when gram equivalents have reacted. This energy term should not be confused with the ordinary heat of reaction which is represented with the symbol $-\Delta H$ by physical chemists. The Q used in this discussion means the energy term which is represented by $-\Delta F$ in textbooks of physical chemistry. E is in volts, and F = 96,500 coulombs if Q is expressed in volt-coulombs (watt-seconds). If, however, Q is expressed in gram calories, F = 23,066. If Q' represents the energy liberated when n equivalents react, the equation becomes

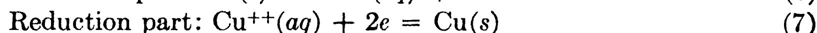
$$Q' = nFE \tag{4a}$$

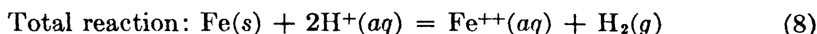
force that makes the oxidation-reduction reaction take place; it is a measure of the tendency of the reaction to proceed or of how complete the reaction must be before a condition of equilibrium is attained.

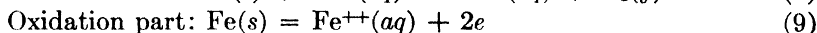
Electrode Reactions (Half Reactions).—As has already been indicated, every oxidation-reduction reaction may be divided into two parts: one part showing the loss of electrons (oxidation) and the other showing the gain of electrons (reduction). Reactions (1), (2), and (3) and the following examples will serve as illustrations:

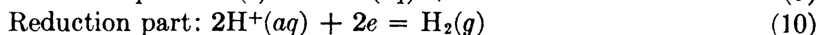

Total reaction: $Fe(s) + Cu^{++}(aq) = Fe^{++}(aq) + Cu(s)$ (5)


Oxidation part: $Fe(s) = Fe^{++}(aq) + 2e$[1] (6)

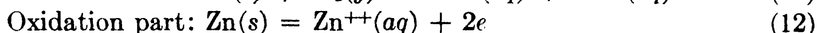

Reduction part: $Cu^{++}(aq) + 2e = Cu(s)$ (7)

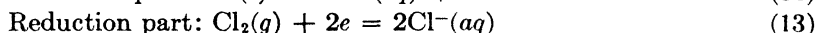

Total reaction: $Fe(s) + 2H^{+}(aq) = Fe^{++}(aq) + H_2(g)$ (8)

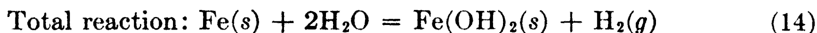

Oxidation part: $Fe(s) = Fe^{++}(aq) + 2e$ (9)

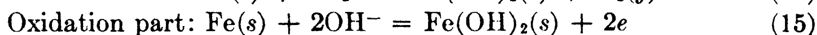

Reduction part: $2H^{+}(aq) + 2e = H_2(g)$ (10)

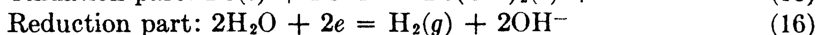

Total reaction: $Zn(s) + Cl_2(g) = Zn^{++}(aq) + 2Cl^{-}(aq)$ (11)


Oxidation part: $Zn(s) = Zn^{++}(aq) + 2e$ (12)


Reduction part: $Cl_2(g) + 2e = 2Cl^{-}(aq)$ (13)


Total reaction: $Fe(s) + 2H_2O = Fe(OH)_2(s) + H_2(g)$ (14)


Oxidation part: $Fe(s) + 2OH^{-} = Fe(OH)_2(s) + 2e$ (15)


Reduction part: $2H_2O + 2e = H_2(g) + 2OH^{-}$ (16)

These half reactions representing the oxidation part and the reduction part of a complete oxidation-reduction reaction represent the changes that occur at the electrodes in a galvanic cell, or in an electrolysis cell. They usually are called *electrode reactions* or *single electrode reactions.* At the anode, electrons are continually being given to the external circuit (oxidation is taking place) and at the cathode, electrons from the external circuit are being consumed to reduce some substance. To avoid confusion, one always should define the anode as the electrode at which oxidation occurs, and the cathode as the electrode at which reduction takes place.

[1] The symbol *e* may be used to represent a single electron or a mole (Avogadro's number = 6.02×10^{23}) of electrons. Thus Eq. (6) may be read: "One atom of iron forms a ferrous ion in aqueous solution and two electrons" or "One mole (gram atomic weight) of solid iron forms a mole of ferrous ions in aqueous solution and two moles of electrons." When a mole of electrons has passed through an external circuit, a Faraday of electricity (96,500 coulombs) has passed.

Most persons are familiar with anode reactions that, like reactions (9) and (12), involve the oxidation of a free metal to form the simple positive ion of the metal in solution. In any study of corrosion reactions due to galvanic couples, however, it is important to recognize that the metal ions formed at anodic areas frequently encounter some ion in the solution with which they will precipitate an insoluble compound of the metal. All the metals that are important as engineering materials form hydroxides and oxides which are quite insoluble in water and in aqueous solutions near the neutral point.[1] Some of these oxides and hydroxides become less soluble as the solution becomes more alkaline, a few which are amphoteric[2] in character become soluble in strongly alkaline solutions, and most of them are soluble in solutions containing a sufficient amount of the proper acid.

The more common cases of corrosion involve metals in contact with water which is either neutral, or only slightly acid, or slightly basic. Therefore the metal ions produced by oxidation of the metal at anodic areas usually find OH^- ions at sufficient concentration in the aqueous solution to precipitate a hydroxide or oxide as the corrosion product on or near to the anodic areas. This type of process is represented by Eq. (14). Although the primary anode

[1] Water itself dissociates slightly into hydrogen and hydroxyl ions, $H_2O \rightleftharpoons H^+ + OH^-$, and in water or in any aqueous solution, the concentrations of H^+ and OH^- must be such that they satisfy this equilibrium: $C_{H^+} \times C_{OH^-} = 1.0 \times 10^{-14}$ (ion product of water). In pure water and in neutral solutions $C_{H^+} = C_{OH^-} = 1.0 \times 10^{-7}$ mole per liter. If the C_{OH^-} in a solution is increased by adding a base, C_{H^+} must correspondingly be decreased to satisfy the ion product of water. Thus if $C_{OH^-} = 0.1$ mole per liter, $C_{H^+} = (1 \times 10^{-14})/0.1 = 1 \times 10^{-13}$ mole per liter. In like manner, if C_{H^+} is increased by adding an acid, C_{OH^-} must be decreased to satisfy the ion product of water. If $C_{H^+} = 0.01 = 1 \times 10^{-2}$ mole per liter, $C_{OH^-} = (1 \times 10^{-14})/(1 \times 10^{-2}) = 1 \times 10^{-12}$ mole per liter. A convenient and commonly used scheme for expressing the acidity or alkalinity of a solution is by stating the pH of the solution: $pH = \log \frac{1}{C_{H^+}}$. If in a solution, $C_{H^+} = 10^{-3}$ mole per liter, $pH = \log \frac{1}{10^{-3}} = 3$. For a neutral solution $pH = 7$; when $pH < 7$, the solution is acid and when $pH > 7$ the solution is alkaline.

[2] Amphoteric hydroxides are those which may dissociate either as an acid or as a base. Example: $Zn(OH)_2(s) \rightleftharpoons Zn^{++} + 2OH^-$ (dissociation as a base); $Zn(OH)_2(s) \rightleftharpoons 2H^+ + ZnO_2^{--}$ (dissociation as an acid). In acid solutions $Zn(OH)_2$ acts as a base and dissolves, $Zn(OH)_2(s) + 2H^+(aq) + 2Cl^-(aq) = Zn^{++}(aq) + 2Cl^-(aq) + 2H_2O$ but in sufficiently alkaline solutions, it acts as an acid and also dissolves, $Zn(OH)_2(s) + 2Na^+(aq) + 2OH^-(aq) = 2Na^+(aq) + ZnO_2^{--}(aq) + 2H_2O$.

reaction may be written



$$Fe(s) = Fe^{++}(aq) + 2e \quad (17)$$

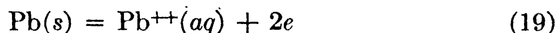
it is followed by the reaction



$$Fe^{++}(aq) + 2OH^{-}(aq) = Fe(OH)_2(s) \quad (18)$$

and $Fe(OH)_2$ is precipitated on or adjacent to the anodic areas. It is customary therefore to write the complete anodic reaction as the sum of the above two reactions, yielding Eq. (15).

In some cases negative ions other than the OH^- ion are present in the solution in sufficient amounts to bring about the precipitation of the compound of the metal ion with the other negative ion. For example, when metallic lead, exposed to sulfuric acid solution, behaves as an anode (the lead plate in the discharge of a lead storage battery) the primary anode reaction may be written



$$Pb(s) = Pb^{++}(aq) + 2e \quad (19)$$

but Pb^{++} ions quickly encounter SO_4^{--} ions in sufficient concentration to precipitate finely divided $PbSO_4(s)$ over the anode surface



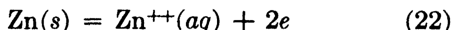
$$Pb^{++}(aq) + SO_4^{--}(aq) = PbSO_4(s) \quad (20)$$

Usually, therefore, the anode reaction in the discharge of the lead storage cell is written as the sum of Eqs. (19) and (20).



$$Pb(s) + SO_4^{--}(aq) = PbSO_4(s) + 2e \quad (21)$$

When zinc is attacked by solutions of the proper pH and CO_2 content, the solid corrosion product is the carbonate rather than the hydroxide. In this case the anodic processes may be written



$$Zn(s) = Zn^{++}(aq) + 2e \quad (22)$$



$$Zn^{++}(aq) + CO_3^{--}(aq) = ZnCO_3(s) \quad (23)$$

or



$$Zn(s) + CO_3^{--}(aq) = ZnCO_3(s) + 2e \quad (24)$$

The reduction of metal ions to form free metal is a common cathode reaction, Eq. (3), but the cathode reactions most frequently encountered in corrosion processes are either (1) the reduction of hydrogen ions to form hydrogen gas, or (2) the reduction of oxygen gas at the cathode to form hydroxyl, OH^-, ions.



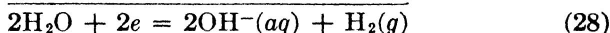
$$2H^+(aq) + 2e = H_2(g) \qquad (25)$$



$$2H_2O = 2OH^-(aq) + 2H^+(aq) \qquad (26)$$



$$2H^+(aq) + 2e = H_2(g) \qquad (27)$$



$$2H_2O + 2e = 2OH^-(aq) + H_2(g) \qquad (28)$$

If the solution is acid, one usually writes Eq. (25) to represent the formation of hydrogen gas on the cathode areas. However, if the solution is neutral or alkaline and the hydrogen ions must come from the dissociation of water molecules, the cathode process is probably best represented by the steps indicated by Eqs. (26) and (27). The sum of these two steps yields Eq. (28), which frequently is written to represent the cathodic production of hydrogen gas in neutral or alkaline solutions.

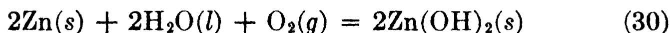
The cathodic reaction whereby oxygen gas is reduced to hydroxyl ions at the cathode areas may be represented by the equation



$$O_2(g) + 2H_2O + 4e = 4OH^-(aq) \qquad (29)$$

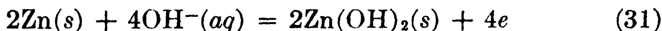
It is sometimes assumed that the primary electrochemical step in the reduction of oxygen at a cathode is the discharge of hydrogen, Eqs. (25) to (28), but that oxygen, if present, will react with the hydrogen atoms ($4H + O_2 = 2H_2O$) before they can combine with each other and be evolved as hydrogen gas, $H + H = H_2(g)$. As shown by Eqs. (26) to (28), the discharge of hydrogen ions results in the production in solution of an equivalent quantity of hydroxyl ions.

When metallic zinc is attacked by water in the presence of oxygen or air, a solid corrosion product of $Zn(OH)_2$ is deposited on the surface of the metal. The total corrosion reaction is



$$2Zn(s) + 2H_2O(l) + O_2(g) = 2Zn(OH)_2(s) \qquad (30)$$

At the anode areas, zinc is oxidized in the electrode reaction

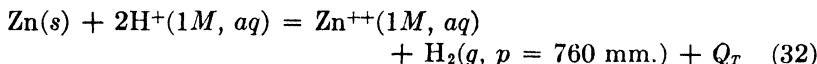


$$2Zn(s) + 4OH^-(aq) = 2Zn(OH)_2(s) + 4e \qquad (31)$$

Oxygen is reduced at the cathode areas by reaction (29). Obviously, the sum of Eqs. (31) and (29) is the over-all corrosion reaction represented by Eq. (30).

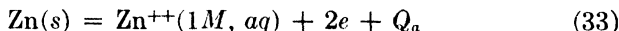
Single Electrode Potentials.—Just as we may divide a total oxidation-reduction reaction into two half reactions, so we may divide the total energy liberated in the reaction between the half reactions.

Total reaction:



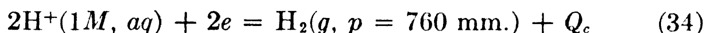
$$Zn(s) + 2H^+(1M, aq) = Zn^{++}(1M, aq) + H_2(g, p = 760 \text{ mm.}) + Q_T \quad (32)$$

Anode reaction:



$$Zn(s) = Zn^{++}(1M, aq) + 2e + Q_a \quad (33)$$

Cathode reaction:



$$2H^+(1M, aq) + 2e = H_2(g, p = 760 \text{ mm.}) + Q_c \quad (34)$$

Since Eq. (33) added to (34) yields (32)

$$Q_T = Q_a + Q_c \quad (35)$$

$$Q_T = nFE_T; \qquad Q_a = nFE_a; \qquad \text{and} \qquad Q_c = nFE_c \quad (36)$$

Hence

$$E_T = E_a + E_c \quad (37)$$

E_T may be measured or it may be calculated from Q_T. It seems impossible to obtain an absolute value for E_a or E_c, but accurate relative values are obtained by arbitrarily assigning a value of zero to E_c for the electrode reaction represented by Eq. (34) when the active concentration of hydrogen ion in the solution is one mole per liter and the hydrogen gas on the electrode surface is at a pressure of 1 atm. (760 mm. Hg). This means that we are assigning a potential of zero to the electrode consisting of a noble metal (for example, platinum covered with platinum black) whose surface is kept saturated with hydrogen gas at a pressure of 1 atm. immersed in a solution containing hydrogen ions at an active concentration of one mole per liter. This standard hydrogen electrode reaction may be combined with other electrode reactions to make complete galvanic cells whose voltages (E_T) may be measured. E_T then becomes E_a for the other electrode compared to the standard hydrogen electrode. For example, the reversible E_T for the galvanic cell in which (32) is the reaction is 0.762 volt.

$$E_T = 0.762 = E^\circ(Zn = Zn^{++} + 2e) + E^\circ(2H^+ + 2e = H_2)$$

Inasmuch as we have arbitrarily made

$$E^\circ[2H^+(1 \text{ mole per l.}) + 2e \rightleftharpoons H_2(g, 1 \text{ atm.})] = 0.000,$$

$E^\circ[Zn(s) = Zn^{++}(1 \text{ mole per l.}) + 2e] = +0.762$ volt. This represents the potential, relative to the standard hydrogen electrode,

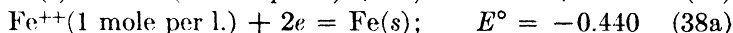
of a pure unstrained zinc electrode in contact with a solution containing zinc ions at an active concentration of one mole per liter. It is called the standard single electrode potential of zinc.

By setting up galvanic cells in which various standard electrode reactions are combined with the standard hydrogen electrode, the standard single electrode potentials corresponding to the various electrode reactions may be determined. If the potentials correspond to the electrode reactions in the direction in which electrons are lost, they also may be called standard oxidation potentials because they represent the tendency of some substance to be oxidized to a more positive valence by losing electrons.

The potential corresponding to the reverse process (gain of electrons) is called a reduction potential. The standard oxidation potential and the standard reduction potential for an electrode reaction are the same numerically but are opposite in sign. For example,



$$Fe(s) = Fe^{++}(1 \text{ mole per l.}) + 2e; \qquad E^\circ = +0.440 \qquad (38)$$



$$Fe^{++}(1 \text{ mole per l.}) + 2e = Fe(s); \qquad E^\circ = -0.440 \qquad (38a)$$

A fairly comprehensive list, including most of the standard oxidation potentials for electrode reactions encountered in corrosion problems, is given in Table 71.

The more positive (or less negative) the standard potential, the greater the tendency of the electrode reaction to proceed in the direction in which electrons are lost. The convention that has been used concerning the sign of the electrode potential is just the opposite from that used by many practical electrochemists who are more interested in the sign of the charge on an electrode than in the significance of the electrode potentials as indicators of the energy change accompanying the electrode reaction. The sign used in Table 71 and in this discussion is in agreement with that used by the majority of physical chemists and theoretical electrochemists in America. Furthermore it is the convention used in most standard textbooks and reference books[1] in this country. It usually is possible to eliminate any controversy over the sign of electrode potential by saying that an electrode is a certain number of volts more anodic (or less anodic) than the standard hydrogen electrode. Thus, the zinc-zinc ion electrode is 0.762 volt more

[1] See, for example, "International Critical Tables," McGraw-Hill Book Company, Inc., New York. LATIMER, "Oxidation Potentials." Prentice-Hall Inc., New York (1938).

anodic than the standard hydrogen electrode. The copper-cupric ion electrode is 0.3448 volt less anodic (or 0.3448 volt more cathodic) than the standard hydrogen electrode.

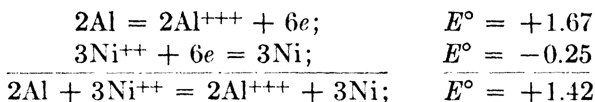
TABLE 71.—STANDARD OXIDATION POTENTIALS

Electrode reaction	$E°$	Electrode reaction	$E°$
$Na = Na^+ + e$	2.712	$Co = Co^{++} + 2e$	0.277
$Mg + 2OH^- = Mg(OH)_2(s) + 2e$	2.67	$Ni = Ni^{++} + 2e$	0.250
$Mg = Mg^{++} + 2e$	2.34	$Cu + 2OH^- = Cu(OH)_2(s) + 2e$	0.224
$Al + 3OH^- = Al(OH)_3(s) + 3e$	2.31	$Sn = Sn^{++} + 2e$	0.136
$Al = Al^{+++} + 3e$	1.67	$Pb = Pb^{++} + 2e$	0.126
$Mn + 2OH^- = Mn(OH)_2(s) + 2e$	1.47	$Fe = Fe^{+++} + 3e$	0.036
$Mn + CO_3^{--} = MnCO_3(s) + 2e$	1.35	$H_2(g) = 2H^+ + 2e$	0.000
$Cr + 3OH^- = Cr(OH)_3(s) + 3e$	1.3	$Cu + CO_3^{--} = CuCO_3(s) + 2e$	−0.053
$Zn + 2OH^- = Zn(OH)_2(s) + 2e$	1.245	$Hg + 2OH^- = HgO(s) + H_2O + 2e$	−0.0984
$Zn + CO_3^{--} = ZnCO_3(s) + 2e$	1.07	$2Hg + 2OH^- = Hg_2O(s) + H_2O + 2e$	−0.123
$Mn = Mn^{++} + 2e$	1.05	$Ag + Cl^- = AgCl(s) + e$	−0.2222
$3Fe + 8OH^- = Fe_3O_4(s) + 4H_2O + 8e$	0.91	$2Hg + 2Cl^- = Hg_2Cl_2(s) + 2e$	−0.2676
$Fe + 2OH^- = Fe(OH)_2(s) + 2e$	0.877	$2Ag + 2OH^- = Ag_2O(s) + H_2O + 2e$	−0.344
$H_2(g) + 2OH^- = 2H_2O + 2e$	0.828	$Cu = Cu^{++} + 2e$	−0.3448
$Cd + 2OH^- = Cd(OH)_2(s) + 2e$	0.815	$4OH^- = O_2(g) + 2H_2O + 4e$	−0.401
$Cd + CO_3^{--} = CdCO_3(s) + 2e$	0.80	$4OH^- = O_2(g, p = 0.21 \text{ atm.}) + 2H_2O + 4e$	−0.391
$Zn = Zn^{++} + 2e$	0.762	$2Ag + CO_3^{--} = Ag_2CO_3(s) + 2e$	−0.47
$Fe + CO_3^{--} = FeCO_3(s) + 2e$	0.755	$Cu = Cu^+ + e$	−0.522
$Fe + 3OH^- = Fe(OH)_3(s) + 3e$	0.73(?)	$2Hg = Hg_2^{++} + 2e$	−0.7986
$Co + 2OH^- = Co(OH)_2(s) + 2e$	0.73	$Ag = Ag^+ + e$	−0.7995
$Cr = Cr^{+++} + 3e$	0.71	$2H_2O = O_2(g) + 4H^+(10^{-7} \text{mole/l}) + 4e$	−0.815
$Ni + 2OH^- = Ni(OH)_2(s) + 2e$	0.66	$Hg = Hg^{++} + 2e$	−0.854
$Co + CO_3^{--} = CoCO_3(s) + 2e$	0.63	$Pt = Pt^{++} + 2e$	−1.20
$Pb + 2OH^- = PbO(s) + H_2O + 2e$	0.578	$2H_2O = O_2(g) + 4H^+ + 4e$	−1.229
$Pb + CO_3^{--} = PbCO_3(s) + 2e$	0.506	$2Cl^- = Cl_2(g) + 2e$	−1.3583
$Ni + CO_3^{--} = NiCO_3(s) + 2e$	0.45	$Au = Au^{+++} + 3e$	−1.42
$Fe = Fe^{++} + 2e$	0.440	$2F^- = F_2(g) + 2e$	−2.85
$H_2(g) = 2H^+(10^{-7} \text{mole/l}) + 2e$	0.414		
$Cd = Cd^{++} + 2e$	0.402		
$2Cu + 2OH^- = Cu_2O(s) + H_2O + 2e$	0.361		
$Pb + SO_4^{--} = PbSO_4(s) + 2e$	0.355		

An examination of the table will reveal that the electrode reactions involving free metals forming their simple positive ions in solution stand in the order of the familiar *displacement* or *electromotive force series:* Na, Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, H_2, Cu, Hg, Ag, Pt, Au. Any metal will displace from aqueous solution the ions of a metal below it in the series. Any metal with a positive standard potential can displace hydrogen ions from a solution containing them at a concentration of one mole per liter or higher. Examples already have been given in Eqs. (1), (5), and (8). Of all the substances listed in Table 71, metallic sodium

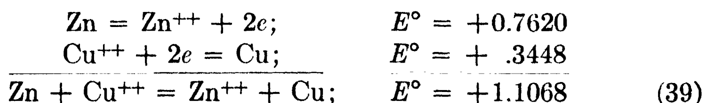
($E^\circ = +2.712$) is the best reducing agent (most easily oxidized) and fluoride ion ($E^\circ = -2.85$) is the poorest reducing agent. If the sign of the electrode potential is changed, it is a measure of the tendency of the electrode reaction to proceed in the reverse direction; *i.e.*, it is a measure of the oxidizing power of the substance that appears on the right-hand side of the equation in the table. Thus fluorine gas is the best oxidizing agent, since $F_2(g) + 2e = 2F^-$, $E^\circ = +2.85$ volts, and sodium ion is the poorest oxidizing agent with $E^\circ = -2.712$ for $Na^+ + e = Na$.

Standard Electromotive Force of Cells and Standard Electrode Potentials.—The combination of two of the single electrode reactions listed in the table, one in the direction given and the other in the reverse direction, will constitute a complete oxidation-reduction reaction. In some cases it is necessary to multiply one or both of the electrode reactions by a factor to make the electrons lost in the anode reaction equal to the electrons gained in the cathode reaction. For example, in the displacement of Ni^{++} ion by aluminum, the anode reaction $Al = Al^{+++} + 3e$ must be multiplied by 2, and the cathode reaction, $Ni^{++} + 2e = Ni$, must be multiplied by 3.



$$\begin{array}{ll} 2Al = 2Al^{+++} + 6e; & E^\circ = +1.67 \\ 3Ni^{++} + 6e = 3Ni; & E^\circ = -0.25 \\ \hline 2Al + 3Ni^{++} = 2Al^{+++} + 3Ni; & E^\circ = +1.42 \end{array}$$

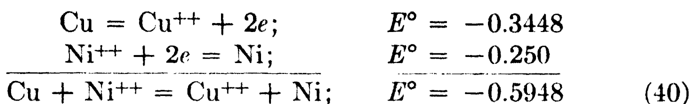
It should be noted that even though the electrode reaction is multiplied by a factor, E° for the electrode reaction remains unchanged, because E° depends upon the energy change per gram equivalent. The sum of the electrode potentials would be the reversible voltage of the galvanic cell (couple) in which the oxidation-reduction reaction was occurring. This total reversible voltage will be a measure of the *driving force* in the reaction and hence of how complete the reaction can be before equilibrium is reached and the couple is completely discharged. For example, the standard voltage of the Daniell cell may be obtained by adding



$$\begin{array}{ll} Zn = Zn^{++} + 2e; & E^\circ = +0.7620 \\ Cu^{++} + 2e = Cu; & E^\circ = +\ .3448 \\ \hline Zn + Cu^{++} = Zn^{++} + Cu; & E^\circ = +1.1068 \end{array} \qquad (39)$$

The positive sign of E° for the complete couple means that the reaction is spontaneous; *i.e.*, that the galvanic couple actually could

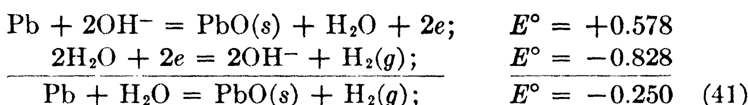
supply electrical energy. If $E°$ for a cell is negative in sign, it means that the proposed reaction is not spontaneous and that electrical energy would have to be supplied from a source outside the system. As an example of the latter, consider



$$\begin{array}{rl} Cu = Cu^{++} + 2e; & E° = -0.3448 \\ Ni^{++} + 2e = Ni; & E° = -0.250 \\ \hline Cu + Ni^{++} = Cu^{++} + Ni; & E° = -0.5948 \end{array} \quad (40)$$

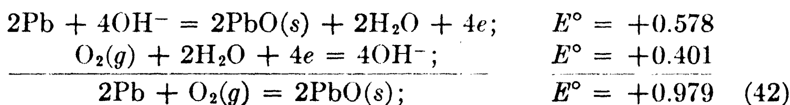
The proposed reaction is not spontaneous; *i.e.*, metallic copper cannot displace nickel ions from solution, indeed the reverse reaction is well known to be spontaneous.

Suppose one wished to know whether lead in the presence of pure water and in the absence of oxygen would spontaneously corrode to form $PbO(s)$ and H_2 gas as corrosion products, the answer could be obtained from our table of electrode potentials as follows:



$$\begin{array}{rl} Pb + 2OH^- = PbO(s) + H_2O + 2e; & E° = +0.578 \\ 2H_2O + 2e = 2OH^- + H_2(g); & E° = -0.828 \\ \hline Pb + H_2O = PbO(s) + H_2(g); & E° = -0.250 \end{array} \quad (41)$$

We may therefore state that lead in contact with pure water could not corrode to form solid PbO and evolve $H_2(g)$ against atmospheric pressure. One might next ask whether lead could corrode to form $PbO(s)$ if oxygen at atmospheric pressure were admitted to the system.



$$\begin{array}{rl} 2Pb + 4OH^- = 2PbO(s) + 2H_2O + 4e; & E° = +0.578 \\ O_2(g) + 2H_2O + 4e = 4OH^-; & E° = +0.401 \\ \hline 2Pb + O_2(g) = 2PbO(s); & E° = +0.979 \end{array} \quad (42)$$

From these data, it is evident that the corrosion of lead in the presence of oxygen would be a very spontaneous reaction.

Influence of Concentrations upon Cell Voltages.—It seems logical that the amount of energy liberated in a chemical reaction should depend upon the concentrations of the reactants and upon the concentrations at which the products are being formed. This must be true because the potential or free energy of any substance in solution is increased as its concentration is increased, and the amount of energy liberated in a reaction increases as the concentrations of reactants increase and as the concentrations of products decrease. Applied to the case of the galvanic cell, this means that the voltage of the cell will increase as the concentrations of reactants increase and the concentrations of products decrease.

In the Daniell cell reaction, $Zn(s) + Cu^{++} = Zn^{++} + Cu(s)$, this principle tells us that the cell voltage would increase as $C_{Zn(s)}$ and $C_{Cu^{++}}$ are increased, and as $C_{Zn^{++}}$ and $C_{Cu(s)}$ are decreased. However, the concentrations of the solid metals are fixed and the voltage will depend upon $C_{Zn^{++}}$ and $C_{Cu^{++}}$. To give this cell a high voltage, a low $C_{Zn^{++}}$ and a high $C_{Cu^{++}}$ are necessary. When $C_{Zn^{++}} = C_{Cu^{++}} = 1.0$ mole per liter, the potential of the Daniell cell is +1.1068 volts [see Eq. (39)]. As current is taken from the cell, the $C_{Zn^{++}}$ will increase due to oxidation of metallic zinc and the $C_{Cu^{++}}$ will decrease because Cu^{++} ions are reduced to metallic copper. Hence as the cell is discharged, its reversible (max.) voltage gradually will drop.

If one represents any galvanic cell reaction by



$$aA + bB = fF + gG \tag{43}$$

the reversible voltage at 25°C. may be expressed in terms of $E°$ for the cell and the concentrations by the equation[1]

$$E = E° - \frac{0.05915}{n} \log \frac{(C_F)^f(C_G)^g}{(C_A)^a(C_B)^b} \tag{44}$$

in which a represents the moles of A, b the moles of B, etc., and n represents the number of Faradays of current that pass through the external circuit when a moles of A react with b moles of B. An entirely similar equation gives the single electrode potential in terms of the standard electrode potential and the concentrations of the substances involved in the electrode reaction. Any electrode becomes less anodic as the concentrations of the products of the electrode reaction are increased and as the concentrations of the reactants are decreased.

Polarization in Galvanic Cells.—The galvanic cell or couple potentials which have been the subject of the discussion up to this point have been reversible potentials; *i.e.*, potentials when all of the potential or free energy liberated in the reaction is converted into electrical energy. All processes for the conversion of energy from one form into another become less efficient as the speed of the conversion is increased, increasing portions of the available energy being dissipated as heat. This applies to the galvanic cell. If current is taken from a cell at a rapid rate, only a fraction of the

[1] For a more detailed discussion of this equation, its applications, and the subject matter of this section, see Getman and Daniels, "Outlines of Theoretical Chemistry," 6th ed., pp. 414–440, John Wiley & Sons, Inc., New York, or any other standard text in physical chemistry or electrochemistry.

energy liberated in the cell reaction is converted into electrical energy and the voltage drops. The difference between the reversible (maximum) voltage and the actual voltage is called *polarization*, A dissipative effect is sometimes referred to as an *irreversible effect*, or a *back-* or *counter-electromotive force.*

It is convenient and instructive to classify the various dissipative or irreversible effects as follows:

1. Dissipation due to the resistance of the electrolyte between anodic and cathodic areas. This is equal to IR_i, where I represents the current flowing and R_i the total resistance of the electrolyte (internal resistance) between the anode and cathode. From Ohm's law this may be set equivalent to a voltage drop. $E'_i = IR_i$

2. Dissipation due to the resistance of the external circuit between anode and cathode. This also may be set equal to a voltage, $E'_e = IR_e$. This effect is very small in corrosion problems because the corrosion couple is essentially a short-circuited cell, the resistance of the metal, R_e, between anodic and cathodic areas being very small.

3. Polarization at the anode. The total anodic polarization is the sum of (*a*) concentration polarization at the anode, (*b*) a possible anodic overvoltage due to some slow process in the over-all anodic reaction, and (*c*) the resistance of films that may cover the anode surface. This sum may be expressed as a back electromotive force, E'_a, called the total anodic polarization.

4. Polarization at the cathode which is usually the sum of (*a*) concentration polarization at the cathode, (*b*) cathodic overvoltage due to a slow step in the over-all cathode reaction, and (*c*) the resistance of films on the cathode surface. The last is a much less frequent contributor to cathodic polarization than it is to anodic polarization. E'_c may be used to denote this sum at the cathode expressed as a back electromotive force and called the total cathodic polarization.

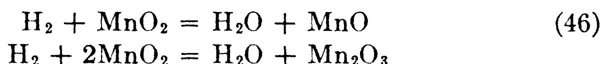
Concentration Polarization.—The concentrations of substances right at the electrode are those which determine the potential of an electrode. It should be evident that as electrode reactions proceed the concentrations in the immediate vicinity of the electrode will be different from those in the main body of the electrolyte, because as the process continues ions or molecules must diffuse away from or into the film adjacent to the electrode. These concentration gradients which are set up about the electrodes when a cell or couple is discharged at an appreciable rate cause a back electromotive force

which is called *concentration polarization.* For example, when a dry cell[1] is discharged, zinc ions are formed about the zinc electrode and as their concentration is increased the zinc become less anodic. To minimize concentration polarization, ammonium chloride is used in the electrolyte to remove zinc ions by the reaction



$$Zn^{++} + 4NH_4Cl \rightleftharpoons [Zn(NH_3)_4]^{++} + 4HCl \qquad (45)$$

Hydrogen ions are discharged at the carbon cathode to form hydrogen gas resulting in a depletion of hydrogen ions about the cathode, which therefore becomes less cathodic. Also, as hydrogen ions are discharged, the pressure of H_2 gas on the cathode increases to cause additional concentration polarization. Polarization due to this source is partly counteracted by packing manganese dioxide about the cathode. This substance, called a "depolarizer," reacts with H_2 and keeps its pressure low on the cathode.

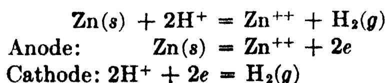


$$H_2 + MnO_2 = H_2O + MnO \qquad (46)$$
$$H_2 + 2MnO_2 = H_2O + Mn_2O_3$$

In addition to the concentration polarization due to the accumulation of H_2 at the cathode, there is another source of polarization in this case; namely, the overvoltage for the discharge of hydrogen ions at the cathode surface.

Overvoltage or Overpotentials.—Even though one eliminated the possibility of concentration polarization at an electrode, one still would find a polarization effect in many electrode reactions. Anodic or cathodic polarization which cannot be attributed to concentration polarization or film resistances is called *overvoltage* or *overpotential.* Overvoltages may be of considerable magnitude, especially in electrode reactions that involve gases, the discharge of hydrogen or the reduction of oxygen gas at cathodes, or the discharge of oxygen, chlorine, etc., at anodes. In general, overvoltages in electrode reactions involving the metals and their

[1] The dry cell contains a zinc anode and a carbon cathode upon which hydrogen is liberated. The cathode, therefore, is essentially a hydrogen electrode. The fundamental cell reaction is



$$Zn(s) + 2H^+ = Zn^{++} + H_2(g)$$
$$\text{Anode:} \quad Zn(s) = Zn^{++} + 2e$$
$$\text{Cathode:} \quad 2H^+ + 2e = H_2(g)$$

ions are quite small. Overvoltages[1] depend upon the following variables:

1. The current density (amperes per unit area of cathode or anode surface). Overvoltage increases rapidly at first with current density, but finally attains a maximum value at high current densities.

2. Overvoltage decreases with increase in temperature.

3. The magnitudes of the gas overvoltages depend upon the nature of the electrode. For example, hydrogen overvoltages are low on Pt, Au, and Ag, intermediate on Fe, Ni, Co, C, and Cu, and high on Pb, Zn, Cd, and Hg.

4. Gas overvoltages are lower on rough, abraded metal surfaces than on smooth, polished surfaces.

5. Overvoltages may be increased by the addition of suitable substances to the electrolyte. For example, hydrogen overvoltages are increased by the addition of such substances as glue, gelatin, and the types of substances used as inhibitors (page 429) in acid pickling.

Polarization Due to Films.—Films on an anode or cathode surface, separating these areas from the main body of the electrolyte, will increase the anodic or cathodic polarization for two principal reasons: (1) they cause an increase in the resistance of the path between anode and cathode, and (2) they decrease the rate of diffusion of reactants and products of the electrode reactions toward and away from the electrode surfaces, thereby increasing concentration polarization to values that may be much higher than those which would prevail in the absence of the films.

The more adherent and nonporous the film, the more it will serve to increase the polarization at an electrode, but even porous, loosely adhering films may exert a pronounced effect. As will become evident in the later discussion, these films, whether they are naturally formed on metal articles during manufacture, are formed by application of special coatings, or consist of corrosion products, will play an important role in determining the rate of attack of an environment upon a metal or an alloy.

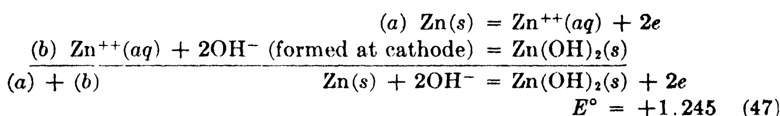
The Spontaneity of Corrosion Reactions.—It is always important to know whether a specific metal can spontaneously react with a specific environment. For example, for many years much time

[1] For a more detailed discussion of overvoltage and other aspects of polarization see Creighton and Kohler, "Electrochemistry," Vol. I, pp. 250–275, John Wiley & Sons, Inc., New York (1935); Glasstone, "Textbook of Physical Chemistry," pp. 994–1023, D. Van Nostrand Company, Inc., New York (1940).

was spent in debating the question, "Can pure iron react with pure water if oxygen is absent from the system?" Today it is possible to answer such questions with certainty in most cases because data usually are available that permit a calculation of the change in potential energy (free energy) accompanying the proposed reaction. As has been indicated (page 407), the reversible electromotive force or driving force of the corresponding corrosion couple may be calculated from the energy change. If the calculated voltage is positive, the proposed reaction can occur; if it is negative, the corrosion reaction is impossible under the conditions postulated. The limitations of space prohibit giving the results of such calculations for a great variety of metals in a large number of environments. It is instructive, however, to list the results for a number of common metals on the assumption that they corrode to form solid corrosion products in two of the most common environments: (*a*) in water with oxygen absent, and (*b*) in water saturated with air (assuming air contains 21 per cent of oxygen, $p_{O_2} = 0.21$ atm. = 159.6 mm. Hg). If a metal corrodes in oxygen-free water, hydrogen must be displaced; therefore this type of corrosion will be referred to as "hydrogen type." Corrosion in water in the presence of oxygen will be called "oxygen type." These types will be illustrated using zinc as an example.

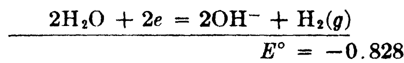
If the corrosion of zinc is of the hydrogen type:

At anode areas:



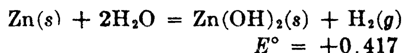
$$(a)\quad Zn(s) = Zn^{++}(aq) + 2e$$
$$(b)\quad Zn^{++}(aq) + 2OH^- \text{ (formed at cathode)} = Zn(OH)_2(s)$$
$$(a) + (b)\qquad Zn(s) + 2OH^- = Zn(OH)_2(s) + 2e \qquad E^\circ = +1.245 \quad (47)$$

At cathode areas:



$$2H_2O + 2e = 2OH^- + H_2(g) \qquad E^\circ = -0.828$$

Total corrosion reaction:

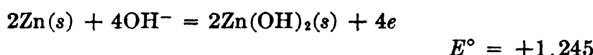


$$Zn(s) + 2H_2O = Zn(OH)_2(s) + H_2(g) \qquad E^\circ = +0.417$$

The calculation shows that zinc can corrode in pure oxygen-free water to form solid zinc hydroxide and hydrogen gas. The driving force of the corrosion couple is +0.417 volt, which corresponds to a liberation of potential energy equivalent to 9,622 cal. for every gram equivalent weight of zinc that corrodes.

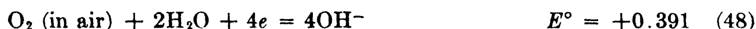
In the presence of oxygen, the changes at the anode areas would be the same as in the foregoing example.

At anode areas:



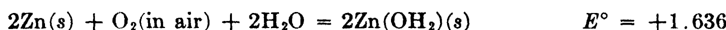
$$2Zn(s) + 4OH^- = 2Zn(OH)_2(s) + 4e \qquad E^\circ = +1.245$$

At cathode areas:



$$O_2 \text{ (in air)} + 2H_2O + 4e = 4OH^- \qquad E^\circ = +0.391 \qquad (48)$$

Total corrosion reaction:



$$2Zn(s) + O_2\text{(in air)} + 2H_2O = 2Zn(OH_2)(s) \qquad E^\circ = +1.636$$

It is evident that the corrosion of zinc in water saturated with air is a much more spontaneous reaction than in pure water. However, the calculation shows that the corrosion of zinc is a quite spontaneous process even when oxygen is excluded from the water.

TABLE 72.—SPONTANEITY OF CORROSION REACTIONS

Metal	Solid corrosion product	Hydrogen type		Oxygen type	
		E $p_{H_2} = 1.0$ atm.	Q, cal. per g. mole of metal	E $p_{O_2} = 0.21$ atm.	Q, cal. per g. mole of metal
Mg	$Mg(OH)_2$	+1.84	85,100	+3.06	142,000
Al	$Al(OH)_3$	+1.48	102,570	+2.70	180,700
Mn	$Mn(OH)_2$	+0.64	29,660	+1.86	85,800
Cr	$Cr(OH)_3$	+0.47	32,700	+1.69	117,000
Zn	$Zn(OH)_2$	+0.417	19,260	+1.636	75,200
Fe	Fe_3O_4	+0.082	4,990	+1.30	79,800
Fe	$Fe(OH)_2$	+0.049	2,260	+1.268	58,500
Cd	$Cd(OH)_2$	−0.013	−600	+1.206	55,600
Fe	$Fe(OH)_3$	−0.098	−6,780	+1.12	77,800
Co	$Co(OH)_2$	−0.098	−4,520	+1.12	51,700
Ni	$Ni(OH)_2$	−0.168	−6,760	+1.05	48,500
Pb	PbO	−0.250	−11,550	+0.969	44,500
Cu	Cu_2O	−0.467	−10,780	+0.752	17,400
Cu	$Cu(OH)_2$	−0.604	−27,900	+0.615	28,400
Hg	HgO	−0.926	−42,600	+0.293	13,600
Hg	Hg_2O	−0.951	−21,970	+0.268	6,190
Ag	Ag_2O	−1.172	−27,070	+0.047	1,080

It is interesting to note that of the metals listed in Table 72, Mg, Al, Mn, Cr, Zn, and Fe can corrode to form a solid corrosion product (water is saturated with the oxide or hydroxide) even in the absence of oxygen. Iron can corrode in oxygen-free water to

form ferrous hydroxide or to form magnetite, Fe_3O_4, but cannot form ferric hydroxide. The corrosion reaction leading to the formation of Fe_3O_4 is the more spontaneous, and it is interesting to point out that recent investigations[1] show quite conclusively that magnetite is the final solid product of the corrosion of iron in oxygen-free water. The other metals in the list cannot corrode in oxygen-free water, but all the metals listed can corrode spontaneously in water saturated with air.

The data in Table 72 emphasize one important aspect of the whole corrosion problem; namely, since the corrosion of almost every metal in the presence of water containing oxygen is spontaneous, the real problem is one of understanding the factors that control the rate of discharge of the galvanic corrosion couples so that steps may be taken when possible to decrease the corrosion rate.

Anode and Cathode Areas in Corrosion Couples.—It is important to recognize the factors that cause certain areas of an exposed metallic structure to be anodic to other areas of the structure. The anodic areas, of course, are the areas attacked, because it is here that metal is oxidized. As will be emphasized later, there is no advantage in limiting the anodic areas unless the total amount of corrosion is correspondingly decreased, since a limitation in area without a proportionate decrease in the amount of corrosion would lead to "pitting."

The principal factors that, alone or in combination, determine which areas will be anodic and which cathodic may be summarized as follows:[2]

Anodic Areas	Cathodic Areas
1. Strained metal	1. Unstrained metal
2. Areas at which there is a low oxygen concentration	2. Areas where oxygen concentration is high
3. Areas at which a protective film has been broken	3. Impurities in the metal upon which there is a low oxygen or low hydrogen overvoltage
4. Impurities in metal or in electrical contact with metal which are anodic to the metal	4. Impurities in metal or in contact with metal which are cathodic to the metal

[1] COREY and FINNEGAN, *Proc. A.S.T.M.*, **39**, 1242 (1939). See discussion to this paper by J. C. Warner. THOMPSON, *Trans. Electrochem. Soc.*, **78**, 251 (1940).

[2] For an excellent and more complete summary of these factors see Mears and Brown, *Ind. Eng. Chem.*, **33**, 1001 (1941).

The Limiting Corrosion Rate.—The reversible voltage of the corrosion couple may be considered the driving force of the corrosion reaction. As has been mentioned, each of the dissipative effects, which together make up the total polarization, increases as the amount of current flowing between anodic and cathodic areas is increased. If, therefore, corrosion proceeds by an electrochemical mechanism (by the discharge of galvanic couples), one may conclude that the steady-state corrosion rate will be the rate that makes the sum of all the dissipative effects, expressed as counterelectromotive

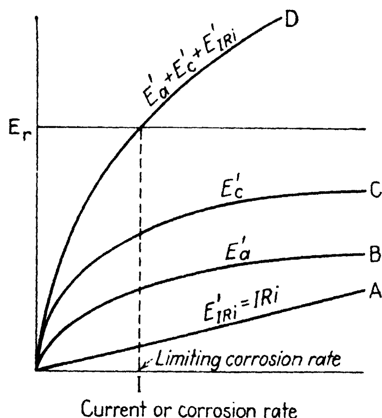


Fig. 85.—Factors determining the limiting corrosion rate.

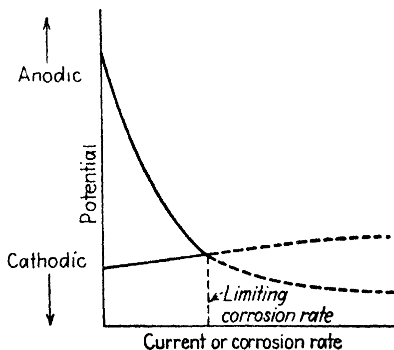


Fig. 86.—Corrosion process under anodic control.

forces, equal to the driving force. Hence, for the steady state, one may write:

$$E_r = E'_a + E'_c + E'_{IR_i} + E'_{IR_e} \tag{49}$$

where

E_r = reversible electromotive force of the couple (Table 72).

E'_a = total polarization at the anode areas.

E'_c = total polarization at the cathode areas.

E'_{IR_i} = IR_i = current flowing × resistance of electrolyte between cathode and anode areas.

E'_{IR_e} = IR_e = current flowing × resistance of the metal between cathode and anode areas. This resistance, R_e, ordinarily is very small and hence E'_{IR_e} may be neglected in most cases.

The significance of the limiting corrosion rate may be demonstrated graphically by reference to Fig. 85. Curve *D* repre-

sents the sum of A, B, and C. When corrosion proceeds at a rate corresponding to a current I flowing between anodic and cathodic areas, the sum of the irreversible or dissipative effects (total polarization) is equal to the driving force of the corrosion couple. Therefore, a rate corresponding to the current I will be the steady-state corrosion rate if the character of the over-all corrosion reaction is not changed. From the diagram, it should be evident that anything that will increase the resistance of the electrolyte, increase the total anodic polarization, or increase the cathodic

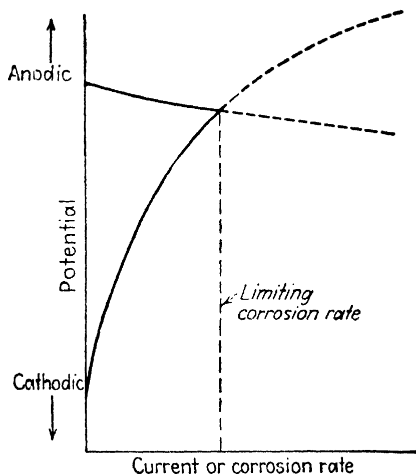


FIG. 87.—Corrosion process under cathodic control.

polarization, will decrease the corrosion rate. This conclusion is very useful in any endeavor to find a means of decreasing the corrosion rate in a given system.

In most cases E'_c and E'_a are large compared to E'_{IR_i}, and one may consider that polarization makes anode areas less anodic and cathode areas less cathodic. Thus, as polarization increases, the two areas are being brought more nearly to the same potential. If E_{IR_i} may be neglected, the corrosion rate that will yield sufficient polarization to bring the anodic and cathodic areas to the same potential will be the limiting corrosion rate. This scheme is illustrated in Figs. 86, 87, and 88.

The difference between the potential of the anode and the cathode at zero current represents the reversible electromotive force or driving force of the corrosion couple. As the rate of discharge of the couple is increased, the potentials (including

polarization) of the anode and cathode approach each other, and become equal at the limiting or steady-state corrosion rate. If E_{IR_i} has an appreciable value, the corrosion rate is set at a lower limit; namely, the rate at which E_{IR_i} is equal to the difference between the anodic and cathodic curves. In Fig. 88, I represents the limiting rate if E_{IR_i} is very small, but I' is the limiting rate when $E_{IR_i} = AB$.

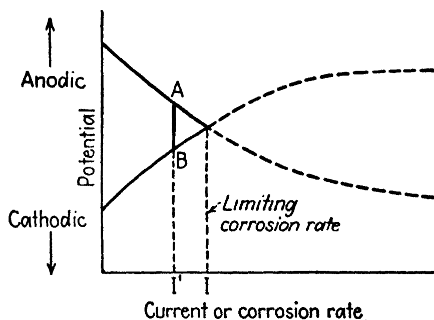


FIG. 88.—Corrosion process under mixed control.

Anodic Control and Cathodic Control.—If, as is illustrated in Fig. 86, anodic polarization is the predominant dissipative effect, the corrosion process is said to be under "anodic control." The case illustrated in Fig. 87 obviously is under "cathodic control." Figure 88 represents an example of "mixed control" in which anodic and cathodic polarizations are comparable in magnitude. In any attempt to apply protective measures it usually is important to recognize the type of control that prevails in the unprotected case.

In the attack of zinc by acids leading to hydrogen evolution, the process is most certainly under cathodic control, the overvoltage for hydrogen evolution at cathode areas being the most important contributor to the total polarization.

The corrosion of partly immersed low-carbon steel in pure water or neutral salt solutions in the presence of air, also is under cathodic control. The areas just below the water-air interface are cathodic and the surfaces immersed to greater depths are anodic. That the corrosion rate is determined by the rate at which oxygen can reach the cathodic areas by diffusion (oxygen concentration polarization at the cathode) is demonstrated by the fact that the weight loss is essentially the same for specimens of equal width immersed to different depths. With all depths of immersion of like samples, the cathodic area remains essentially the same; *i.e.*, the area just

below the interface which can be reached by oxygen diffusing into the liquid from the atmosphere. As the depth of immersion is increased, the anodic area is increased, but in spite of the increased anodic area, the weight loss remains the same because the process is under cathodic control.

If increasing the anodic area causes no appreciable increase, but a restriction in the cathode area causes a decrease in the corrosion rate, one concludes that the process is under cathodic control. On the other hand, a process in which the corrosion rate is essentially independent of the cathode area but decreases as the anodic area decreases is under anodic control.

The corrosion of aluminum, stainless steels, and other metals and alloys that form adherent, quite nonporous films on their surfaces in many common environments provides examples of processes that are under anodic control.[1]

Inhibitors and Intensity of Attack.—Any substance that, when added to the environment of a metal or alloy, decreases the corrosion rate is called an *inhibitor.* As the names imply, *anodic inhibitors* decrease the rate by impeding the anodic process and *cathodic inhibitors* serve to increase the total polarization at cathode areas. The use of chromates, phosphates, silicates, etc., to decrease the rate of corrosion of iron and other metals serves as examples of anodic inhibition. These substances in general serve to help form or keep in repair a protective film on the metal surface. The addition of calcium, magnesium, zinc, or nickel salts will decrease the rate of corrosion of iron and steel under conditions of partial immersion. At the cathodic areas near the water line, the alkalinity is increased as oxygen is reduced, leading to a precipitation of $Mg(OH)_2$, $Zn(OH)_2$, or $Ni(OH)_2$ over the cathodic surface as a more or less adherent, porous deposit. To reach the cathodic surface, oxygen must diffuse through these deposits and its rate of arrival is therefore decreased. To make calcium salt additions effective, the solution must contain carbonate or bicarbonate ion so that $CaCO_3$ will precipitate in the region of high alkalinity about the cathode. These substances function, therefore, as cathodic inhibitors.

Another important class of cathodic inhibitors are the organic substances which decrease the rate of acid attack on metals in such processes as pickling. These are discussed in more detail in a later paragraph.

[1] Benson, Brown, and Mears, *Trans. Electrochem. Soc.*, **76**, 259 (1939).

It must be emphasized that the successful use of inhibitors frequently requires considerable knowledge of their action and a thorough understanding of the corrosion process in the system under consideration. Substances that may successfully decrease the rate of attack on a metal, or stop it entirely, in one environment may in another environment stimulate corrosion. In still other environments the inhibitor, although decreasing the over-all corrosion rate, may bring about an increase in the intensity of attack at restricted anodic areas, leading to pitting and rapid perforation.

Oxygen, depending upon conditions, may act as an inhibitor or a stimulator of corrosion. Oxygen tends to make a surface cathodic because it is a reactant in the cathodic reaction in oxygen-type corrosion, and also because it, in many cases, helps keep in repair a passivating oxide film. It has been definitely shown[1] that the higher the oxygen concentration at a metal surface, the lower the probability of attack on iron or steel. However, once weak points are attacked, the rate of attack will be stimulated by increasing the oxygen concentration.

The prevention of localized corrosion or pitting is obviously more important than bringing about a decrease in the over-all corrosion rate. Failures rarely are due to moderate corrosion spread over large areas; they usually result from intense attack on small, localized areas leading to pitting and early perforation. For this reason one must consider the influence of an inhibitor on the area attacked of equal importance to its influence upon the over-all corrosion rate. Inhibitors that may increase the intensity of attack are classed as dangerous. In general, intensification of attack results when the anodic areas are very small and the process is under cathodic control. This situation frequently results when an insufficient concentration of an anodic inhibitor is added to a system in which the corrosion process is under cathodic control. For example, the addition of insufficient chromate to completely stifle oxygen type corrosion of iron, steel, zinc, and aluminum, has been shown to cause serious intensification of the attack. The use of still larger amounts of chromates in these cases usually will bring the process under anodic control and give almost complete protection. It is important to mention that the amount of chromate necessary to eliminate pitting and give protection will depend

[1] EVANS and MEARS, *Proc. Roy. Soc.* (*A*), **146**, 164 (1934); *Trans. Faraday Soc.*, **31**, 527 (1935).

upon the concentration of such ions as sulfate and chloride, in the aqueous medium. These ions interfere with the formation of passivating films on the metal.

Mears[1] divides inhibitors into three classes:

1. *Dangerous Inhibitors.*—Those which reduce the total corrosion but reduce the area attacked still more rapidly, so that the intensity is increased.

2. *Safe Contractive Inhibitors.*—Those which reduce the area attacked but reduce the total corrosion still more rapidly, so that the intensity is decreased.

3. *Safe Expansive Inhibitors.*—Those which reduce the total corrosion but increase the area attacked, so that for two reasons the intensity is decreased.

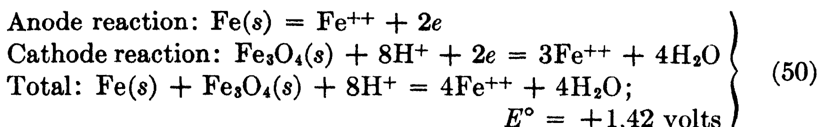
Inhibitors in Acid Pickling of Iron and Steel.—Properly to prepare the surface of iron and steel for galvanizing, tinning, enameling, electroplating, etc., it is necessary to remove the scale that is formed in the hot-working operations. The usual method for scale removal is acid pickling. In recent years organic-type inhibitors have been quite universally used to decrease acid attack on the basis metal leading to hydrogen evolution, without appreciably altering the rate of scale removal.

From the investigations of Pilling and Bedsworth[2] and of Pfeil[3] we learn that the normal scale formed on iron and steel consists of three layers: an outer layer which is approximately Fe_2O_3, a middle layer of Fe_3O_4, and a layer next to the iron which is approximately FeO in composition. The FeO phase decomposes on slow cooling, at about 575°C. (1065°F.) into Fe_3O_4 and microscopic or submicroscopic particles of iron. Such a decomposed phase, produced in the normal cooling of scale, is vigorously attacked by even dilute acids. If, however, the scale has been rapidly quenched, or if the decomposed phase has been annealed for about an hour at 500 to 550°C. (930 to 1020°F.) to permit growth of the iron particles, it is only slowly attacked by even strong acids. When the normally cooled ferrous material is dipped into the pickling acid, there appear to be three spontaneous reactions involving the hydrogen ion from the acid which may go on by electrochemical mechanisms:

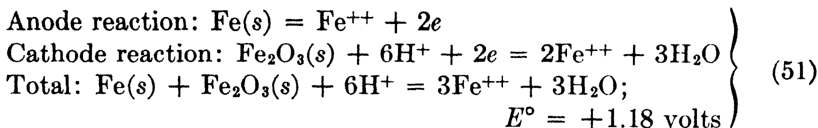
[1] See Mears' discussion to paper by Evans, *Trans. Electrochem. Soc.*, **69,** 213 (1936).

[2] Pilling and Bedsworth, *J. Inst. Metals*, **29,** 529 (1923); *Ind. Eng. Chem.*, **17,** 372 (1925).

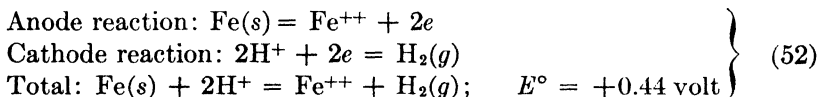
[3] Pfeil, *J. Iron Steel Inst.*, **119,** 501 (1929); **123,** 237 (1931).



$$\left.\begin{array}{l}\text{Anode reaction: } Fe(s) = Fe^{++} + 2e \\ \text{Cathode reaction: } Fe_3O_4(s) + 8H^+ + 2e = 3Fe^{++} + 4H_2O \\ \text{Total: } Fe(s) + Fe_3O_4(s) + 8H^+ = 4Fe^{++} + 4H_2O; \\ \qquad\qquad E^\circ = +1.42 \text{ volts}\end{array}\right\} \quad (50)$$



$$\left.\begin{array}{l}\text{Anode reaction: } Fe(s) = Fe^{++} + 2e \\ \text{Cathode reaction: } Fe_2O_3(s) + 6H^+ + 2e = 2Fe^{++} + 3H_2O \\ \text{Total: } Fe(s) + Fe_2O_3(s) + 6H^+ = 3Fe^{++} + 3H_2O; \\ \qquad\qquad E^\circ = +1.18 \text{ volts}\end{array}\right\} \quad (51)$$



$$\left.\begin{array}{l}\text{Anode reaction: } Fe(s) = Fe^{++} + 2e \\ \text{Cathode reaction: } 2H^+ + 2e = H_2(g) \\ \text{Total: } Fe(s) + 2H^+ = Fe^{++} + H_2(g); \quad E^\circ = +0.44 \text{ volt}\end{array}\right\} \quad (52)$$

The first two reactions lead to scale removal and some iron oxidation. The finely divided iron in the decomposed FeO phase is likely to be the first oxidized because of its higher activity and its dispersion throughout the Fe_3O_4 matrix. As long as scale is close to the basis metal, it seems likely that reactions (50) and (51) will be predominant over reaction (52). They are more spontaneous, and polarization effects accompanying their cathode reactions are almost certain to be much lower than the polarization for hydrogen deposition. It seems logical to assume that only when appreciable areas (at least microscopic areas) of basis metal are exposed does the acid attack on iron (leading to hydrogen evolution) begin.

The rate of acid attack on the basis metal is undoubtedly controlled by the cathodic polarization for hydrogen evolution and cathodic inhibitors may be added to the pickling acid which will greatly decrease or even practically eliminate the acid attack on the basis metal. It is believed that inhibitors function in this case by being adsorbed on the metal surface to form a fairly well organized and oriented film which serves to increase the polarization for hydrogen evolution by increasing the hydrogen overvoltage or by introducing a high transfer resistance[1] between the solution and the metal surface.

The decrease in acid attack on iron caused by the presence of organic inhibitors probably was first reported in 1872. Since that time at least 150 organic substances have been shown to possess

[1] Chappell, Reotheli, and McCarthy, *Ind. Eng. Chem.*, **20**, 582 (1928). Warner, *Trans. Electrochem. Soc.*, **55**, 287 (1929). Warner, *Metal Cleaning, Finishing*, **10**, 104 (1938).

inhibiting properties. These materials cover the range from cabbage leaves, bran, extracts and residues from organic processes, sludge acids from petroleum refineries, and coal-tar products, in which the active ingredient may not be known, to highly complex synthetic organic chemicals of definitely known structure and composition. In general, organic compounds that possess inhibitor properties will be found to contain nitrogen, oxygen, sulfur, or other elements in the fifth and sixth periodic groups. The property is possessed particularly by aliphatic and aromatic amines and their derivatives, heterocyclic nitrogen compounds (pyridine and quinoline) and their derivatives, substitution products of urea and thiourea, mercaptans, organic sulfides, aldehydes, ketones, and some organic acids. The inhibitor may be truly soluble in the pickling acid or may be colloidally dispersed (gelatin and glue). It seems evident that an inhibitor must consist of a hydrocarbon part attached to a polar or ionizable group. The systematic studies[1] on the relation between structure and inhibitor effectiveness should be consulted by the reader interested in the subject.

The properties desired in an inhibitor have been summarized by Warner.[2] It should be pointed out that in the selection of the most suitable inhibitor for a given purpose, only plant trials will give the final answer. However, many laboratories have devised tests[3] which will select the few out of the hundreds that are worthy of such a trial.

Importance of Films on Metals.—As has been mentioned, the attack of an environment upon a metal or an alloy usually leads to the formation of a corrosion product which is insoluble in the environment. The film of corrosion product tends to stifle the corrosion process by increasing anodic polarization, cathodic polarization, or the resistance between anodic and cathodic areas. The protective power of a film is a relative term depending upon all the existing conditions. A film that affords excellent protection in one environment may be quite useless in a different set of circumstances. One encounters films that afford all intermediate degrees of protection from that offered by a spongy mass, which merely hinders the diffusion of reactants and products (most films formed at cathodic areas are of this type), to that given by

[1] MANN *et al.*, *Ind. Eng. Chem.*, **28**, 159 (1936); *Trans. Electrochem. Soc.*, **69**, 115 (1936). RHODES and KUHN, *Ind. Eng. Chem.*, **21**, 1066 (1929).

[2] WARNER, *Metal Cleaning, Finishing*, **10**, 104 (1938).

[3] MUNGER, *Trans. Electrochem. Soc.*, **69**, 85 (1936).

highly organized, adherent, practically nonporous and insoluble films that cause the metal or alloy to become completely passive.

All metals, except the very noble metals, when exposed to air at room temperature, or at higher temperatures, in the process of manufacture or fabrication, are attacked by oxygen to form an oxide film on the surface. If the oxide has a lower specific volume than the metal, the film must shrink and crack, providing channels for the further rapid access of oxygen to the metal. Such films are not protective and should be expected in the case of the alkali and most of the alkali earth metals (lithium, sodium, potassium, calcium, strontium, barium, etc.).

When, however, the oxide has a higher specific volume than the metal, the oxide film will be formed under compression and, at temperatures that are not too high, the metal will be completely covered and the protection may be complete when the film has grown to only a few molecular layers in thickness. Films of this type are formed on copper, brass, tin, lead, iron, nickel, Monel metal, stainless steel, zinc, chromium, aluminum, and many other metals and alloys when they are exposed to relatively dry air. These films are responsible for the relative permanence of these metals and alloys under atmospheric exposure. When the temperature of exposure is high enough so that the film can continue to grow by the diffusion of oxygen or of metal through the film, the film usually will wrinkle and crack due to the strain. A common example is found in the scaling of iron and steel at higher temperatures. Such films no longer offer much protection and the metal continues to oxidize. This explains the fact that the films that give complete protection by making the metal *passive* are invariably very thin films. Indeed, passivating films, originally postulated by Faraday, are so thin that they are ordinarily invisible. Only recently through the investigations of Evans[1] have these films been isolated and made visible. Although passivating films are most commonly produced when metals are exposed to air, they are formed in some cases in attack by aqueous mediums. As examples, one may cite the passivating films formed on iron in concentrated nitric acid; on iron in solutions containing sufficient chromate, permanganate, or hydrogen peroxide; on stainless steel in most aqueous solutions; on aluminum in most aqueous solutions; on copper in chromate solutions; etc.

[1] EVANS, "Metallic Corrosion, Passivity and Protection," pp. 48–94, Edward Arnold & Co., London (1937).

The behavior of a metal or alloy, with its air-formed film, when it is brought into contact with water or an aqueous solution will depend to a great extent upon the effect of the aqueous medium on the character of the film. The air-formed film, due to impurities in the metal, mechanical damage, or other chance variations, will develop weak spots. If the environment is such that film defects are kept in repair, the film will continue to afford protection. If, on the other hand, the environment does not aid in the repair of film defects or causes film deterioration, the protective action is lost and the rate of corrosion will increase with time.

In general, anions that are oxidizing and anions that form very insoluble compounds with the metal tend to aid in film formation and film repair. As examples, one may cite the use of soluble chromates, phosphates, silicates, borates, and hydroxides in proper amounts to give protection to iron and steel in aqueous mediums. Lead becomes passive in sulfuric acid and sulfates owing to the formation of an insoluble adherent film of lead sulfate. The reader will recognize these instances as cases of anodic inhibition. Except for the unusual cases such as iron in concentrated nitric acid, most protective oxide films are destroyed if the aqueous medium is made acid. The presence of many anions such as chloride, bromide, iodide, etc., will cause film breakdown and accelerate corrosion as in the familiar "salt spray" test and in exposure to sea water. It also is interesting to note that lead does not become passive in sulfuric acid containing acetate, nitrate, and a number of other anions that form soluble salts with lead.

The protective film on metals that form amphoteric hydroxides (page 409) may be destroyed if the aqueous medium is made sufficiently alkaline. Thus, zinc, lead, and aluminum are rapidly attacked by alkaline solutions. It is important to note that zinc shows the greatest tendency to become passive in aqueous solutions at a pH of about 10. This is the pH at which zinc hydroxide is least soluble. A useful method for studying the influence of an environment upon film breakdown or film formation has been devised by Burns[1] who plots the potential of the metal in various mediums as a function of the time.

If the film that naturally forms on a metal or alloy before or after exposure is porous, nonadherent, and not strong enough to give protection and if the environment cannot economically be altered to yield a protective film, it frequently is possible to produce

[1] Burns, *J. Applied Phys.*, **8**, 398 (1937).

or apply an artificial film that will give protection. Such films will be the subject of discussion in a later chapter of the text.

Oxygen Concentration Cells. Differential Aeration.—The fact that areas on a metal surface at which the oxygen concentration is low are anodic with respect to areas at which the oxygen concentration is higher already has been mentioned. Corrosion of the less noble metals in many practical cases may be attributed to these differential aeration couples. If a drop of dilute salt solution is placed on an iron surface, the anodic area at which the iron is attacked will be found in the center of the wetted surface; the outer portion of the wetted surface to which oxygen has easiest access will be cathodic and free from attack. Ferrous ions will be produced at the anodic area and hydroxyl ions at the cathodic area; these ions will meet by diffusion in the intermediate region

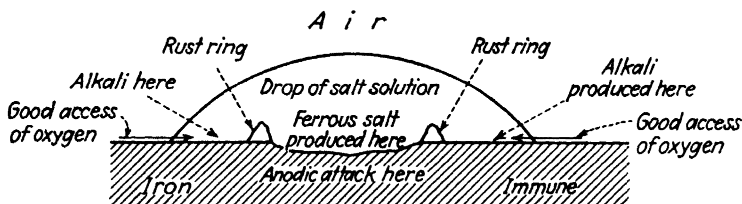


Fig. 89.—Differential aeration type of attack.

and deposit a ring of rust. The situation is well illustrated in Fig. 89.

When iron and various other metals are partly immersed in water that is not agitated, the surface just below the air interface is immune from attack because it is kept cathodic due to the easy access of oxygen to this area. The attack occurs on the areas that are immersed to greater depths. If the aqueous medium is agitated to bring oxygen at equal concentrations to all portions of the surface, anodic and cathodic areas will be determined by other factors.

In totally immersed structures, pitting frequently occurs at areas that are screened from oxygen by deposits of porous corrosion products, dirt, or a variety of solid substances. Thus, wire screens usually corrode at the point of contact between the wires,[1] and pitting has been observed under blocks of wood or pieces of glass resting on metal immersed in aqueous mediums.

[1] McKay and Worthington, "Corrosion Resistance of Metals and Alloys,' p. 28, Reinhold Publishing Corporation, New York (1936).

As a final example, recent measurements[1] may be cited which show that when a zinc plate in contact with a rubber sheet bent to a radius of 1⅝ in. was immersed in aerated tap water, the portion of the sheet in contact with the rubber was about 0.20 volt anodic to the portion of the plate to which oxygen had easy access.

Water-line Attack.—The use of the case of immunity at and immediately below the water line in stagnant water as an example of a differential aeration cell should not be taken as an indication that attack at the water line is a rare occurrence. Indeed, intense attack at the water line is very frequently encountered in a variety of practical circumstances. If the liquid is in motion and contains chlorides and anodic inhibitors such as hydroxide, carbonate, chromate, phosphate, or silicate in insufficient amount to stifle the corrosion reaction completely, the situation[2] is favorable for intense attack at the water line. A variable position for the water line also favors intensification of attack because the porous layer of corrosion product made more compact and adherent when above the liquid medium will, when again submerged, screen the metal surface from oxygen and make that portion of the surface anodic.

Influence of Bacteria on Corrosion.—In a variety of cases it has been demonstrated that certain types of bacteria may influence the corrosion process. Oxygen-consuming bacteria in bodies of water or in soils may bring about a great decrease in the oxygen concentration in the medium in contact with a metal structure. If the structure is entirely exposed to the medium in which the oxygen has been depleted by bacteria, their action may be beneficial. On the other hand, if the structure is only partly exposed to the low-oxygen environment, the bacterial action may lead to intensification of attack due to differential aeration couples.

Certain bacteria (*microspira* or *vibrio desulfuricans*) can, under anaerobic conditions, extract sulfur from sulfates to build up the sulfur-containing albuminous constituents of their protoplasm. In the process, it is supposed that these bacteria can render the oxygen of sulfates into such form that it can act as a depolarizer in the corrosion of iron. The presence of the iron thus assists in the life process of the bacteria by removing one of the products. When these organisms die, sulfur is liberated as hydrogen sulfide, which converts at least a portion of the corrosion product into FeS which is less effective than oxide or hydroxide in stifling the corro-

[1] McKinney and Warner, unpublished data.
[2] Evans, *op. cit.*, pp. 296–298.

sion of iron. This particular type of attack has frequently been encountered with cast iron under anaerobic conditions in the presence of organic matter and sulfates.

The so-called *iron bacteria* appear sometimes to be connected with pitting or pipe blockage due to corrosion products, especially when the water is from boggy districts. These bacteria flourish only in a fairly narrow pH range in the region 5.8 to 7.2, their activity ceasing if the water is made appreciably alkaline. Contrary to a common supposition, iron does not seem to be an essential part of their food, but they do need the organic radicals of the iron salts and deposit the iron as hydrated ferric oxide.

The obstruction of conduits in some circumstances, due to the growth of low-form algae which assimilate iron, also should be mentioned.

Stress Corrosion, Grain Boundary Corrosion, and Corrosion Fatigue.—Internal stresses due to such operations as cold working and quenching, and stresses due to applied loads will, in general, make a metal or alloy more anodic and tend to increase the rate of corrosion unless the process is decidedly under cathodic control. The frequent early failure of strained metals in corrosive environments, however, cannot be attributed to the above effect, but rather to the fact that stresses may be highly concentrated about the point of attack and the material fails by cracking. In the absence of corrosion, similar failures by cracking may be initiated by stress concentrations about surface imperfections such as tool marks.

In alloys whose failure by cracking has been initiated by corrosion, the failure is usually along grain boundaries. It is generally agreed that alloys susceptible to this type of failure contain material in or adjacent to the grain boundaries which is anodic to other grain boundary material or to the main portion of the grain, and that internal stresses in the material contribute to the susceptibility. This hypothesis is supported by measurements[1] of the potentials of grain surfaces and grain boundary materials in various aluminum alloys, by our knowledge of the constitution of susceptible alloys, and by the methods that have been successfully employed to minimize susceptibility.

An alloy might be susceptible to grain boundary corrosion even though the boundary material is not anodic to adjacent material

[1] MEARS and BROWN, *Trans. Electrochem. Soc*, **74**, 495, 519 (1938). DIX, *Trans. A.I.M.E.*, **137**, 11 (1940).

if the boundary material has a decidedly lower tendency than the adjacent material to become passive in the environment.

In general, susceptibility to stress corrosion cracking attack can best be minimized by one or more of the following: (1) by treatments to relieve internal stress, (2) by adjusting composition, including the elimination of certain impurities, to prevent the development of marked differences of composition between the grains and the grain boundary material, and (3) by suitable heat-treatments to prevent the above-mentioned heterogeneity.

The earlier stainless steels were very susceptible to grain boundary corrosion and failure in certain environments due to the fact that the steel adjacent to the grain boundaries was impoverished in chromium by the precipitation from solid solution of carbides richer in chromium than the steel. The regions low in chromium did not possess the same tendency to become passive as the main portion of the grains. This difficulty is overcome by reducing the carbon content of stainless steels to such low values that carbide precipitation does not occur at the grain boundaries, or by adding alloying elements that form very stable carbides (page 371).

The "season cracking" of brass (page 226), long a source of failure in cold-drawn brass articles such as cartridge cases, especially when exposed to environments containing ammonia, can be largely eliminated by a low-temperature anneal (one hour at 275°C. is satisfactory for a $^{70}/_{30}$ brass) to remove internal stresses without appreciable loss of hardness. Brass with not less than 67 per cent of copper is homogeneous, being entirely alpha solid solution. However, the lower copper brasses are heterogeneous, containing some beta solid solution which is anodic to alpha solid solution, and corrodes to lower the zinc content of the alloy. This type of corrosion is known as "dezincification."

The so-called "caustic embrittlement" of boiler plate (page 26) is another example of grain boundary corrosion and failure.

A metal or alloy subjected to alternating stresses may survive a large number of cycles of applied stress and yet finally fracture. The number of cycles needed to cause failure naturally increases as the stress range is reduced and finally, in the absence of a corrosive environment, a lower limit of the stress range is reached below which the specimen will not fail with an infinite number of cycles of applied stress. This is known as the *fatigue strength* or *endurance limit* (page 129), as illustrated in Fig. 90. As illustrated in Fig. 90, there is no endurance limit for a specimen subjected to alternat-

ing stress in a corrosive environment; the curve always falls below that for a like specimen under noncorrosive conditions and the curve never becomes horizontal. This result might easily be predicted since, if corrosion is continued long enough, even with no applied stress, the metal will lose its strength. The term *corrosion fatigue limit* can only mean the stress range below which no fracture would result within some definite number of cycles. If a numerical value of a corrosion fatigue limit is to have meaning, the number of stress cycles must be specified. *Corrosion endurance limit* would seem a better term to use than corrosion fatigue limit.

When corrosion continues in small pores and cracks and the corrosion product has a lower density than the metal, stresses leading

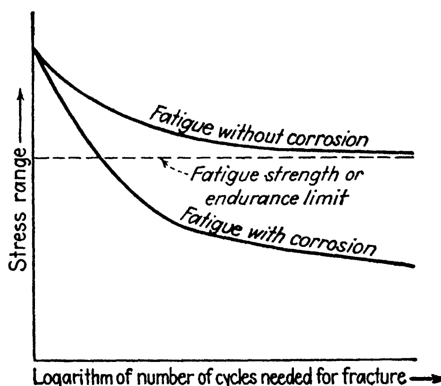


FIG. 90.—Fatigue strength or endurance limit.

to failure may result directly from the corrosion process. Disintegration and swelling by this mechanism are frequently encountered in laminated metallic structures.

Stray Current Corrosion.—Metallic structures such as water and gas pipes and lead cable sheath, adjacent to direct-current circuits, may suffer severe attack due to leakage from the main circuit, a portion of the current flowing through the adjacent structure. The most serious trouble is encountered in the vicinity of trolley lines. Positive current is fed to the overhead trolley and returned through the rails to negative feed points. If the soil in contact with the rails is moist and appreciably conducting, there will be more or less leakage at points to adjacent pipe lines, etc., and at some other point current will return to the rails. At the point of entrance of the current cathodic reactions occur and little damage is done. However, at the point at which current leaves the struc-

ture, anodic reactions involving metal oxidation occur and rapid perforation frequently results. Since cathodic and anodic areas are widely separated, there is less stifling of the corrosion process than normally occurs due to the formation of insoluble substances by reaction between the products of the cathodic and anodic reactions.

To reduce corrosion due to stray currents to a minimum it obviously is necessary to make the resistance of the desired return line (the rail system) as low as possible and the resistance of the undesired return line as high as possible. Good electrical contact between rails and adequate drainage of soil between rails and adjacent pipe lines and structures will produce beneficial results. Any attempt to apply remedial measures should be preceded by a survey[1] of the entire situation by a competent person.

Electrolytic Protection.—Since metal oxidation in corrosion always occurs at anodic areas, it long ago occurred to investigators that one might protect a metallic structure by making the structure cathodic through the use of an externally applied electromotive force. To give complete protection, sufficient current must be passed, with the structure as cathode, to polarize the entire surface up to the potential of the local anodes. Although some important applications have been made, the scheme is not so generally useful as might be expected, because of the difficulties involved in obtaining proper current distribution and because of the cost of the electrical energy consumed when sufficient current is passed to give protection. The reader is referred to other publications[2] for a more detailed discussion of this subject. In spite of the difficulties encountered in providing electrolytic protection, the method has been very useful for protecting pipe lines and other equipment.

Corrosion in Soils.—The enormous investment in underground conduits, water, oil, and gas pipe lines, and other underground metallic structures has stimulated investigations on the relation between the constitution of soils and their corrosive properties. In nonacid soils,[3] the conductivity of a soil, which depends

[1] Knudson, *Trans. Electrochem. Soc.*, **3**, 202 (1903). Evans, *op. cit.*, pp. 23–37.

[2] McKinney, *Trans. Electrochem. Soc.*, **75**, 31 (1939). Evans, *op. cit.*, pp. 27–29, 517–519.

[3] Evans, *op. cit.*, pp. 192–206, 281–282. See also many excellent papers published by the National Bureau of Standards.

upon the moisture and electrolyte content, is the best measure of its corrosive character. In these soils, corrosion usually occurs due to differential aeration couples, and the resistance between anodic and cathodic areas, as well as the rate of oxygen arrival at cathodic areas, will be important in determining the corrosion rate. In highly acid soils, the attack may be of hydrogen type (page 421) with anodic and cathodic areas very close together, the conductivity of the soil being of little importance. In soils high in organic matter, the formation of soluble complex compounds of the metal and the peptizing of corrosion products may prevent the stifling of the corrosion process that would be expected in the absence of the organic matter.

Influence of Contact between Dissimilar Materials.—This subject is of prime importance in considering the corrosion characteristics of galvanized sheet, tin plate, metals and alloys bearing electroplated coatings, cladded materials, structures containing metals or alloys of unlike composition in electrical contact, heterogeneous alloys, soldered and welded structures, etc.

Contact between metallic and nonmetallic materials such as wood, porous corrosion products, glass, and other ceramics is likely to bring about an intensification of the attack on the metallic material due to differential aeration caused by nonmetallic material screening the metallic surface from ready access to oxygen. This subject has already been discussed. We are concerned here primarily with the influence of contact between dissimilar metallic substances upon their corrosion characteristics.

If dissimilar metals in contact are exposed to a corrosive environment in which the more active metal (metal higher in the E.M.F. series, page 414) does not become passive, the more active metal will be anodic and give "cathodic protection" to the less active metal for some distance from the point of contact. The distance to which protection is given will depend upon the conductivity of the environment, the potential of the active metal, the shape and dimensions of the system, and a number of other factors that have not yet been very thoroughly investigated. In most environments, zinc affords such protection to iron and other less active metals, and this accounts for the successful use of galvanized sheet and pipe. Even though a zinc coating is imperfect so that iron is exposed in small areas, the zinc will provide protection for the exposed areas, if they are not too large. In giving protection the zinc, of course, is sacrificed; indeed the attack on zinc usually will

be accelerated by the exposed iron areas. Once the exposed areas are sufficiently large, direct attack on the iron will begin. It has been common practice to insert zinc plugs, rods, or blocks in electrical contact with less active metals to give cathodic protection to boilers, rudders, propellers, brass and bronze valves, and other fittings. The principal problem is one of determining the proper way to locate the zinc so as to distribute the protective current over the entire surface which is to be made cathodic.

A more active metal may not afford cathodic protection to a less active metal if the environment is one in which the active metal tends to become passive and the less active metal remains active. Thus it has been shown that iron becomes anodic to zinc in hot-water heating systems[1] with certain types of water; and iron also becomes anodic to zinc in tap water whose pH has risen to a value of about 10 due to alkali leached from concrete.[2] Zinc will give cathodic protection to more active aluminum and some of its alloys[3] in certain environments. Tin normally is cathodic to iron but in citric acid and in some fruit juices the polarity of this couple may be reversed.

Equally important to giving cathodic protection to a main metal by the sacrificial use of a more active metal, is the influence on the rate of attack, of contact of the main metal with a less active metal. In general, the less active metal will provide the cathodic area and one might expect that the lower its position in the E.M.F. series, the more rapid would be the attack on the main metal. This, however, is not necessarily the case; the most important factor will be the magnitude of the polarization for the cathodic process on the less active metal. If the cathodic polarization on the less active metal is equal or greater than it is on cathodic areas of the main metal, the contact would have little effect upon the corrosion rate, except for the acceleration due solely to the increase in cathodic area. If, on the other hand, the less active metal provides a cathodic surface upon which the polarization is less than on cathodic areas of the main metal, the rate of attack will be accelerated by the contact. These principles may be illustrated with facts concerning the acid attack on zinc leading to hydrogen evolution. Pure zinc is attacked only very slowly because of the high cathodic polarization due to the high hydrogen overvoltage on zinc. Con-

[1] Schikor, *Trans. Electrochem. Soc.*, **76**, 247 (1939).
[2] McKinney and Warner, unpublished results.
[3] Mears and Fahrney, *Trans. A.I.Ch.E.*, **37**, 911 (1941).

tact of zinc with copper, platinum, silver, and nickel will greatly accelerate the attack because of the low hydrogen overvoltage on these metals. On the other hand, contact between zinc and less active metals upon which there is an overvoltage comparable to the high hydrogen overvoltage on zinc (cadmium, lead, and mercury) does not appreciably alter the rate of attack.

In the more common oxygen-type corrosion it is possible to recognize several definite situations and corresponding effects when the main metal is in contact with a less active metal:

1. The process is definitely under anodic control and the rate of attack will be essentially independent of contact with the less active metal and the nature of the less active metal.

2. The process is definitely under cathodic control, but the rate of oxygen arrival at the less active metal cathodic area controls the corrosion rate. Here the rate of attack will be independent of the nature of the less active metal, but may depend somewhat upon the cathodic area.

3. The process is under cathodic control but oxygen has free access to the less active metal cathodic areas. If the polarization for the cathodic process is higher on the less active than on the main metal, the contact will have no appreciable effect on corrosion rate. If, however, the polarization is lower on the less active metal, corrosion of the main metal will be accelerated.

The whole subject of the influence of contact between dissimilar metals and alloys upon corrosion rate is one upon which extensive investigation is urgently needed.

Influence of Temperature on Corrosion Rate.—As should be evident from the preceding discussion, cathodic and anodic polarization, the resistance of the aqueous medium, and diffusion rates largely determine the corrosion rate. As temperature is increased, diffusion rates increase, the conductances of electrolytes increase, and most polarization effects decrease. The corrosion rate therefore usually increases with temperature and corrosion in contact with aqueous mediums or moist air becomes a more serious problem in the warmer climates. The temperature coefficient of corrosion reactions usually is somewhat lower than for ordinary chemical reactions; nevertheless, the acceleration of corrosion by higher temperatures is an extremely important factor. Higher temperatures are important for another reason; a metal or alloy that becomes passive in a certain environment at room temperature may become active in the same environment at higher temperatures. Thus,

although iron becomes passive in concentrated nitric acid at ordinary temperatures, it loses its passivity and goes into solution rapidly if the temperature is raised to 75°C. (167°F.). There are exceptions to this general effect of temperature on corrosion rate; some cases are known in which the corrosion rate decreases with increase in temperature.

Selection of Materials for Specific Uses.—The reader will find much practical information on materials that will withstand specific environments in the treatises by McKay and Worthington, F. N. Speller, and Burns and Schuh, which are mentioned among the accompanying references. Many of the technical and engineering periodicals publish important information to guide the engineer in the selection of his materials of construction. Some of the most useful of these compilations are published from time to time by *Chemical and Metallurgical Engineering.* As an example, the reader is referred to the editorial supplement to the September, 1940, issue of this magazine entitled, "Materials of Construction for Chemical Engineering Equipment."

This discussion of corrosion should be considered merely an introduction to the subject. For further study the following references should be consulted.

References

Burns and Schuh: "Protective Coatings for Metals," Reinhold Publishing Corporation, New York (1939), American Chemical Society Monograph No. 79.

Evans: "Metallic Corrosion, Passivity and Protection," Edward Arnold & Co., London (1937).

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CHAPTER X

PROTECTIVE METALLIC AND INORGANIC COATINGS

By J. C. Warner, Ph.D.

In Chap. IX, the engineering importance of the corrosion of metals and alloys by attack from their environment was emphasized. The reader will recall that one method of affording protection against corrosion is to apply a coating that will resist the environment on the exposed surface of a relatively cheap metal or alloy, which aside from its susceptibility to attack has satisfactory properties as an engineering material. It is more economical, for example, to use tin-coated steel sheet in the manufacture of food containers than to make the cans from any single metal or alloy that will withstand the corrosive action of canned fruits, vegetables, meats, etc. The major portion of the coating industry is devoted to applying suitable coatings to iron and steel because, aside from their susceptibility to corrosion, iron and steel are very economical materials of construction.

These protective coatings may be metallic, inorganic nonmetallic, or organic substances. It is the purpose of this chapter to discuss the most important metallic and inorganic coatings. Organic protective coatings are the subject of a later chapter. Although coatings are used in the vast majority of cases to obtain protection against corrosion, they sometimes are applied for decorative purposes only.

Metallic Coatings

The process of coating or inlaying base metals with gold and silver by hammering the noble metals on the surface of the previously heated base metals is an art of great antiquity. In modern times many methods have been devised for coating one metal with another. The coating of sheet iron by *hot dipping* in tin began about 1600 and galvanizing dates from 1740. The production of Sheffield plate by fusing sheet silver on copper or brass began in 1743. *Cladding* and *fusion welding* are the modern examples of this process. *Dip gilding* or *immersion plating* of silver, gold, or

platinum on base metals was followed by commercial *electrodeposition* or *electroplating* by the use of current in 1840. At the present time coatings of most common metals except aluminum, the alkali and alkali earth metals, can be applied by electrodeposition. The processes of applying metallic coatings by *cementation, spraying,* and *cladding* are developments of the present century.

Preparation of Metal Surfaces for Coating.—It has been truly said that the character of a coating is no better than the surface to which it is applied. As a consequence, the first step in applying a coating, whether it is metallic, inorganic, or organic, is the preparation of the surface of the base metal. This usually involves three steps: the removal of grease and other surface contamination, the removal of oxide scale and corrosion products, and finally an etching treatment to secure adhesion or a buffing and polishing to improve the appearance of the applied coating.

Solvent degreasing,[1] accomplished by using noninflammable chlorinated hydrocarbon solvents such as trichloroethylene in closed systems, is finding wide application. Fatty oils may be removed by saponification with strong alkalies, and mineral oils by emulsification with soaps and other detergents. Immersion in hot alkaline solution is probably the most common cleaning method. In many cases the parts to be cleaned are made cathodic in the alkaline solution with an applied current of about 10 amp. per sq. ft. The vigorous evolution of hydrogen speeds up the degreasing process and also serves to remove some surface scale. Soda ash (sodium carbonate), with small amounts of caustic soda to saponify fatty substances, is the most common constituent of alkaline cleaners, but sodium phosphate, sodium silicate, and borax, alone or in various combinations, frequently are used.

The removal of oxide scale and corrosion products is accomplished by abrasion (grinding, wire brushing, blasting with sand, steel grit, or steel shot) or by acid pickling. Most mill scale is removed from iron and steel by pickling in 4 to 5 per cent sulfuric acid at 65 to 75°C. (150 to 170°F.). Hydrochloric acid is used to a certain extent and a preliminary dip in hydrofluoric acid is sometimes used for sand castings. The use of inhibitors to decrease the acid attack on the metal has been discussed (page 429). Brass and bronze usually are pickled by immersion in mixtures of sulfuric and hydrochloric acid containing a small amount of nitric acid. Iron and steel surfaces that are to be painted are frequently pickled

[1] DAVIDSON, *Trans. Electrochem. Soc.*, **72**, 413 (1937).

in phosphoric acid, or in sulfuric acid followed by a dip in 2 to 10 per cent phosphoric acid.

A final roughening of the surface by etching or abrasion often is practiced when the adhesion of a coating is thereby greatly improved.

Methods Used in Applying Metal Coatings.—Five different methods have found extensive use in the application of metallic coatings and a sixth method is used to a limited extent.

1. *Hot-dip processes* in which the article to be coated is dipped in a bath of molten metal or alloy and then removed after a sufficient time with its adhering film of coating. The metal that forms the coating should have a relatively low melting point because high temperatures would be likely to alter the mechanical properties of the base metal, cause undue contamination of the bath by solution of the base metal, and bring about too extensive penetration and alloying of the coating with the underlying metal. Some alloy formation at the interface between the base and the coating is of course desirable because it promotes adherence. The hot-dipping process is widely used for applying coatings of low-melting metals and alloys such as zinc, tin, lead, terneplate (lead-tin alloy), and solders (page 251).

2. *Electrodeposition or Electroplating.*—In applying metal coatings by electrodeposition, the freshly cleaned base metal is made cathodic in a bath of suitable composition which among other constituents contains in solution a compound of the metal being deposited. The character of the metal deposit depends upon the current density (amperes per unit of cathode area), the temperature, the bath composition, and the presence or absence of "addition agents." The thickness of the deposit depends upon the current density, current efficiency, and the time. If all of the current is being used to deposit metal at the cathode (100 per cent current efficiency), the amount of metal deposited by a given current in a given time may be calculated by Faraday's law (page 407).

In most electroplating processes, anodes of the metal being deposited are used and conditions are adjusted so that metal goes into solution at the anode at the same rate it is being deposited at the cathode, thus maintaining a constant bath composition. As an important exception, it should be mentioned that insoluble anodes (usually lead or lead-antimony alloy) are used in chromium plating, and the bath composition is maintained by the addition of chromic acid at intervals.

With the possible exception of hot dipping for the application of zinc and tin coatings, electrodeposition is the most important method for applying protective metallic coatings of zinc, copper, nickel, tin, chromium, cadmium, lead, silver, gold, and various alloys of controlled composition such as brass, bronze, and "Coronite" (nickel-zinc). Many other metals and alloys are electrodeposited in small amounts for special purposes. For the details of the bath compositions, optimum current densities, temperatures, etc., for obtaining satisfactory deposits of the various metals, the reader must be referred[1] to the larger treatises.

3. *Metal Spraying.*[2]—The method first developed by Schoop about 1910 consists in melting the metal, atomizing the molten metal, and depositing the atomized metal on the surface to be coated. The most commonly used apparatus for metal spraying consists of a lightweight "pistol" which can be held in the hand to direct the stream of metal at will. In most cases the metal is fed through a central barrel in the form of wire. The gaseous mixture of hydrogen, city gas, or acetylene and oxygen, or air, is supplied through a tube surrounding the wire barrel. The gas burning at the orifice melts the protruding part of the wire. Through an outer tube surrounding the gas inlet, compressed air or other gas under pressure is admitted to atomize the molten metal and project it against the surface to be coated.

In another type of pistol, the metal is melted in an electric arc formed between two wires of the metal. In still other types the metal may be supplied in the form of powder or as previously melted liquid metal.

The real advantages of this method of coating are the following: The metal film may be applied to the finished structure in place, may be applied to any desired spot, and being applied to the finished structure, is not subject to further deformation. The thickness of a sprayed coating is controllable between fairly narrow limits and irregular objects can be given a uniform coat more readily than by most other methods.

In general, sprayed coatings are more porous, less adherent, rougher, and harder than coatings applied by other methods. For

[1] BLUM and HOGABOOM, "Principles of Electroplating and Electroforming," 2d ed., McGraw-Hill Book Company, Inc., New York (1930). BURNS and SCHUH, "Protective Coatings for Metals," Reinhold Publishing Corporation, New York (1939). "Metals Handbook," 1939 ed., pp. 1096–1105.

[2] "Metals Handbook," 1939 ed., p. 1115.

satisfactory adherence, it usually is necessary to carefully clean and roughen the surface of the base metal. To obtain comparable protection for ferrous materials from a sprayed coating, it must be somewhat thicker than coatings of the same metal applied by hot dipping or electrodeposition. Their lower density is evidence of the greater porosity of sprayed coatings. This method has been widely used for applying coatings of aluminum, brass, cadmium, copper, lead, Monel metal, nickel, tin, zinc, and various other metals.

4. *Cementation.*[1]—For certain applications a base metal, usually iron or steel, may be protected from corrosion by alloying its surface with another metal by cementation. In this process the articles are packed in the powdered coating metal, or a mixture of the powdered metal and a filler, and are heated at a temperature somewhat below the melting point of the more fusible metal. An alloy layer is formed by diffusion of the coating metal into the base. An inert or reducing (hydrogen) atmosphere usually is provided during the heating period. The method has found some application for producing alloy layers on the surfaces of iron or steel articles with zinc (Sherardizing), chromium (Chromizing), aluminum (Calorizing), and silicon (Siliconizing or Ihrigizing). The casehardening of steel by cementation with carbonaceous materials in the pack carburizing process has been mentioned previously (page 340).

5. *Metal Cladding.*[2]—The early processes for cladding base metals with the noble metals, silver (Sheffield plate), and gold have been mentioned. In recent years, many processes for cladding one metal with another metal or alloy to give corrosion or wear resistance have been developed. These composite materials may be produced in a variety of ways. One method consists of casting a duplex ingot with the coating material on the outside and subsequently rolling the ingot into sheet, bar, or plate, or drawing it into wire. Thus, copper-covered steel articles are made from ingots of copper cast about a steel core in the "Copperweld" process; aluminum alloys are coated with commercially pure aluminum (Alclad) by casting an ingot of the alloy in a steel mold lined with sheet aluminum; tin-coated lead foil is made by rolling a composite ingot obtained by casting tin around a bar of lead; and steel sheet clad with stainless steel may be produced by rolling composite ingots.

[1] Metals Handbook," 1939 ed., pp. 1082–1093. BURNS and SCHUH, *op. cit.*, p. 39.

[2] "Metals Handbook," 1939 ed., pp. 1155–1171. BURNS and SCHUH, *op. cit.*, p. 43.

Another method of cladding involves rolling stacked clean sheets or plates of the two materials, the weld between the materials being obtained in the rolling operation. In other cases the coating sheet is applied by spot welding or resistance welding. Finally, it should be mentioned that some coatings are applied by actually fusing the cladding material over the surface to be coated.

6. *Cathode Sputtering and Condensation of Metal Vapors.*[1]—Although these methods are of little commercial importance compared to those previously discussed, they do appear to be more suitable than other methods for certain limited applications. When a potential of 500 to 2,000 volts is applied between two electrodes in a partial vacuum (0.01 to 0.1 mm. Hg) inducing a glow discharge, the cathode metal undergoes disintegration and is deposited as a thin film on near-by objects in the system. With suitable design of the chamber and proper location of the object to be coated, it is possible to deposit a quite uniform film of the cathode metal. The method is especially useful for depositing thin metallic films on fabrics, phonographic recording waxes, and other materials that are not electrical conductors. It seems certain that in this process the cathode metal is vaporized by local heating due to positive-ion bombardment.

The production of metallic coatings by the condensation of metal vapors produced by heating is closely related to cathode sputtering. The metal, or a crucible containing the metal to be evaporated, is placed in contact with a platimum or tungsten wire heating element in a system evacuated to about 10^{-4} mm. Hg. The metal vapor will condense to form a uniform film on a cool solid surface propery placed in the system.

As another closely related process, the production of metal films by the decomposition of gaseous compounds of the metal should be mentioned. The deposition of nickel by the decomposition of nickel carbonyl is an example.

Zinc Coatings.—Zinc coatings have been applied to base metals, especially iron and steel, for many years to provide protection against corrosion. Zinc being anodic to most base metals gives electrochemical "sacrificial" protection to the base metal by making it cathodic even when the base metal is exposed in small areas. This protection may extend for distances of ¼ in. or more if the aqueous environment has a fairly high electrical conductivity. The first method of applying zinc coatings, *i.e.*, by dipping the base metal in

[1] Burns and Schuh, *op. cit.*, p. 53.

baths of molten zinc (galvanizing), still is most extensively used. However, applications of zinc by electrodeposition from acid zinc sulfate or from potassium zinc cyanide baths, by cementation in zinc dust (Sherardizing), and by spraying have become important processes. Hot-dipped coatings, if properly applied, consist of an inner zone of iron-zinc alloy and an outer layer of almost pure zinc. The coating produced by Sherardizing is almost all iron-zinc alloy, but the coatings produced by spraying are essentially pure zinc. The alloy layer undoubtedly promotes adherence but it is fairly brittle; as a consequence, electrodeposited coatings will usually withstand more deformation without cracking than a hot-dipped coating.

TABLE 73.—ESTIMATED LIFE OF ZINC-COATED PRODUCTS IN THE ATMOSPHERE

Thickness, in. × 1,000	Weight in oz. per sq. ft. of surface*	Life in years under atmospheric conditions					
		Rural	Tropical marine	Temperate marine	Suburban	Urban	Highly industrial
3.6	2.00	50	40	35	30	25	15
2.3	1.25	35	30	25	20	17	9
1.8	1.00	25	20	15	12	10	7
1.1	0.60	10	8	7	5	4	3
0.66	0.37	7	6	5	4	3	2
0.44	0.25	5	4	3	3	2	1

* In the case of galvanized steel sheets, the weight of zinc is specified in terms of total zinc on both sides of the sheet; *i.e.*, a 2-oz. sheet has 1 oz. of zinc per sq. ft. of surface. Consequently, in estimating the life of galvanized sheet in the light of data given in this table, the specified weight and thickness values for the sheet should be halved.

Comprehensive atmospheric exposure tests on zinc coatings conducted by the A.S.T.M.[1] fail to reveal any significant differences in the protection afforded by coatings applied by hot dipping, electrodeposition, or Sherardizing if the coatings are of comparable thickness. In all cases the protection significantly improved as the thickness of the coating was increased. As might be expected, highly industrial atmospheres are the most corrosive, with urban, suburban, temperate marine, tropical marine, and rural atmospheres being less corrosive in the order named. The estimated life of zinc-coated products in the above atmospheres is given in Table 73.

[1] *Proc. A.S.T.M.*, **27**, 191 (1927); **29**, 149 (1929); **31**, 184 (1931); **33**, 156 (1933).

The qualitative character of the estimated life of a coated article should be emphasized. Naturally, failure must be defined in terms of the use to which the article is put; if it is roofing, it may be said to have failed when it become perforated and leaks, whereas fence wire fails only if it breaks. Indoor exposure tests indicate that it is reasonable to expect that the protective life of a zinc coating indoors is at least five times as great as for coatings of the same thickness exposed to outdoor atmosphere in the same locality.

The protection afforded by zinc coatings on articles submerged in aqueous environments, and the life of the coating, will depend upon the oxygen concentration, the pH, the CO_2 concentration, the anions and cations present, and their concentrations. Electrolysis plays a larger part in the performance of coatings in submerged than in atmospheric exposure, and the character of the corrosion products likewise plays an important role. Zinc is not attacked at appreciable rates in pure water free from oxygen and carbon dioxide. In the presence of oxygen, the attack is appreciable but is soon retarded due to the formation of zinc hydroxide and the rate of attack is then controlled by the rate of diffusion of oxygen through the film of corrosion product. Within a certain range of pH, with waters containing carbonates or bicarbonates, the corrosion product will be the basic or normal zinc carbonate. These compounds are more soluble and form a less protective film than zinc hydroxide. Although nitrates, sulfates, and chlorides in small concentrations increase the corrosiveness of water, it is well established that most domestic waters are less corrosive to zinc than distilled water, and hard waters in general are less corrosive than soft waters.

The effect of temperature upon the rate of corrosion of zinc in aerated distilled water has been correlated to the physical character of the corrosion product in several temperature ranges. Up to 50°C. (122°F.) the rate of corrosion increases gradually with temperature and in this range the corrosion products are gelatinous and adherent. Above 50°C. the rate of attack increases rapidly, reaching a maximum at 65°C. (149°F.), and then decreases rapidly at higher temperatures. Between 50 and 65°C., the corrosion product is granular and nonadherent, affording little protection. Above 65°C., the film becomes very dense, adherent, and glossy. These facts undoubtedly explain the corrosion phenomena observed in galvanized pipes and water tanks in hot-water heating systems.

The corrosion of zinc as a function of pH has been studied in some detail[1] with the results shown in Fig. 91. It is evident that the life of a protective zinc coating would be very short except in the pH range 6 to 12.5. As might be expected, the curve for the solubility of amphoteric (page 409) $Zn(OH)_2$ as a function of pH is practically identical with the curve shown in Fig. 91. The general effect of the presence of CO_2 in waters is to displace the curve upward in the figure. For any type of water there is a certain minimum critical thickness of coating below which the protective

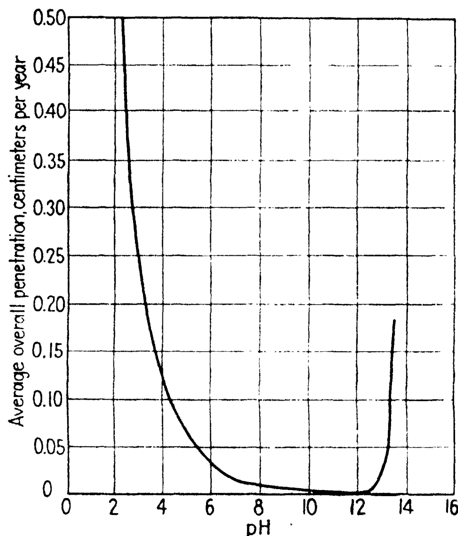


Fig. 91.—Influence of pH on corrosion of zinc.

life of the coating will be very short. An effective coating must be thick enough to provide for the building up of a protective layer of corrosion products before a large percentage of the zinc has been attacked. For the average city water supply, satisfactory protection for iron or steel pipe requires a zinc coating 0.0017 to 0.0020 in. in thickness.

Zinc coatings will give effective protection to iron and many other metals exposed to sea water and other solutions high in chlorides. Indeed in these solutions of high electrical conductivity, the exposed area which will be protected galvanically by zinc is greater than in ordinary water supplies. Zinc has been extensively used in coating steel wires used to support and protect submarine

[1] Rotheli, Cox, and Littreal, *Metals & Alloys*, **3**, 72, (1932).

cable, and to protect marine structures and naval craft. An important recent application has been the cathodic protection[1] of aluminum and aluminum alloys by zinc when subjected to sea-water spray and intermittent immersion in sea water.

Zinc coatings, extensively used on metal articles and structures buried in soils, are subject to the most diverse conditions from place to place or even in one locality from time to time, depending upon the weather. The most extensive study on the corrosion performance of metals in soils has been reported by the National Bureau of Standards.[2] If soils are classed as highly, moderately, or mildly corrosive, the estimated lives of zinc coatings of 1 oz. per sq. ft. will be 1 to 2, 4 to 6, and 18 to 25 yr., respectively.

As has been mentioned, the coating produced in Sherardizing is an iron-zinc alloy. In hot-dip galvanizing an alloy layer is formed between the iron base and the zinc outer coat. These iron-zinc alloys are composed principally of the intermetallic compounds $FeZn_7$ and $FeZn_3$; they are anodic to iron, but less so than pure zinc. They will, therefore, give galvanic protection to exposed base metal, but the protection does not extend over so large an exposed area as would be protected by pure zinc.

In concluding this discussion of zinc coatings it should be mentioned that the ideal situation is one in which the zinc remains just active enough to keep any exposed areas of base metal cathodic. If the environment is such that the zinc becomes passive, the coating will not serve its intended purpose of providing protection. The conditions favoring passivation of zinc so that it becomes cathodic to iron have been discussed previously (page 433).

Tin Coatings.—About 40 per cent of the world's production of tin goes into the manufacture of "tin plate" which is low-carbon steel sheet coated with a thin layer of relatively pure tin. In 1937 the United States produced about 2.5 million long tons of tin plate, which represented over half of the world's production. Almost 60 per cent of the tin plate made in this country is used to produce 17 to 20 billion containers annually for the canning industry. Minor amounts of tin are used for tinning steel and copper wire, copper sheet, cast iron, and various other ferrous and nonferrous articles. The great majority of tin coatings are applied by hot-

[1] Willard and Mears, *Refrig. Eng.*, **40,** 381 (1940). Mears and Fahrney, *Trans. A.I.Ch.E.*, **37,** 911 (1941).

[2] Logan, *J. Research Nat. Bur. Standards*, **17,** 781 (1936). Logan and Ewing, *ibid.*, **18,** 361 (1937).

dipping the cleaned, fluxed articles. In recent years, the application of tin coatings by electrodeposition from acid stannous sulfate or from alkaline stannate baths, and by spraying, has increased in importance.

In the tin-plate industry, the weight of coating is expressed as the weight of tin per "base box." The base box is a unit of area equivalent to 112 sheets, 14 by 20 in. (31,360 sq. in. of sheet or 62,720 sq. in. of surface to be coated). For coatings of 1 lb. per base box, the thickness of tin is 0.000059 in. About 99 per cent of the tin plate produced in this country is the grade known as "coke" plate which has a coating in the range from 1 to 2.5 lb. of tin per base box.

In many respects tin is an excellent coating material. It can be applied as an extremely thin and fairly uniform coating over iron, copper, and other metals; it is fairly resistant to attack by most atmospheres and by aqueous solutions in the absence of oxygen; and tinned sheet can be severely deformed without serious damage to the coating. Tinned surfaces are easily joined by soldering. Foodstuffs are not rendered toxic by contact with tin. However, in most environments, tin is cathodic to iron and does not give the galvanic protection afforded by zinc coatings. The corrosion of tin plate is characterized by rusting at pinholes in the coating; therefore, the obtaining of low porosity is a matter of prime importance in the application of quality coatings.

Owing to the importance of the corrosion characteristics of tin and the tin-iron couple, many investigations[1] of the influence of environment have been reported. Tin is rapidly corroded by alkaline solutions at pH's above 8.5 and by strong acids in the presence of air. In the absence of air the rate of acid attack is very greatly increased by the presence of impurities upon which there is a low overvoltage for hydrogen discharge. The rate of attack in many acid fruit juices is slow, undoubtedly owing to the presence of inhibitors that function in the same manner as the inhibitors used in the acid pickling of iron (page 429). The important fact that tin becomes anodic to iron in certain fruit juices and organic acids, such as citric and oxalic acids, has now been well established.

[1] MANTELL and KING, *Trans. Electrochem. Soc.*, **52**, 435 (1927). LUECK and BLAIR, *ibid.*, **54**, 257 (1928). KOHMAN and SANBORN, *Ind. Eng. Chem.*, **20**, 1373 (1928). HOAR, *Trans. Faraday Soc.*, **30**, 472 (1934). DERGE *et al.*, *Trans. A.I.M.E.*, **128**, 391 (1938); **133**, 294 (1939); *Metals Tech.*, April, 1941.

To prevent blackening of cans due to sulfur compounds in meats and some vegetables, and to prevent the bleaching of certain highly colored fruits, cans are lacquered or enameled on the inside. Beer cans are given two coats of enamel, each coat being baked twice.

Nickel Coatings.—For many years nickel has been used for protective, decorative, and wear-resisting coatings on iron, steel, and brass. Recently nickel, followed by chromium, has been extensively applied to zinc-base die castings used for automobile radiator grilles and hardware. The application of nickel coatings by electrodeposition has always been the most important method. Typical modern nickel-plating baths are composed of nickel sulfate, nickel chloride, and boric acid. The pH of the bath is carefully controlled and the temperature is kept at 50 to 60°C. (122 to 140°F.).

The application of nickel coatings by spraying and by cladding (nickel-clad steel) is increasing in importance. Both spraying and electroplating are finding increased use for building up worn parts with nickel. The wear-resisting properties of nickel have led to its application on electrotypes, propellers, turbine blades, paper machine rolls, etc. Nickel has good corrosion resistance to many common environments. There is practically no attack on nickel by indoor atmospheric exposure; outdoors, the rate of penetration, although varying with atmospheric conditions, is rarely greater than 0.0001 in. per year. Marine atmospheres are not much more corrosive than suburban or rural atmospheres. Nickel is free from stress corrosion in atmospheric exposure.

Nickel is highly resistant to attack by water and most aqueous solutions even though the pH and electrolyte concentration are varied over quite large ranges. Local attack may occur in stagnant sea water under barnacles or other attached nonmetallic materials such as seaweed.

Strong oxidizing acids, such as nitric, corrode nickel rapidly, but cold sulfuric up to 80 per cent, hot sulfuric acid up to 15 per cent, pure phosphoric acid free from oxidizing compounds, dilute cold hydrochloric acid, and organic acids do not seriously attack nickel.

Next to silver, nickel is one of the most resistant metals to strong alkalies. For example, in boiling 50 per cent caustic soda, the rate of penetration is less than 0.001 in. per year. Although dry ammonia does not attack nickel, aqueous ammonia at concentrations above 1 per cent is appreciably corrosive. Nickel resists scaling

in oxidizing atmospheres up to 760°C. (1400°F.), and is also especially useful in the range 1150 to 1260°C. (2100 to 2300°F.).

Nickel, like tin, is cathodic to iron in most environments and does not protect exposed iron by galvanic action. In applying nickel coatings, minimizing porosity is therefore of great importance. The number of pores per unit area in a nickel coating decreases rapidly with increase in thickness; a coating 0.0015 in. in thickness when properly applied is practically pore free. Although various factors influence the porosity of electrodeposited nickel coatings, it has been demonstrated that smooth base-metal surfaces and absence of suspended matter in the plating bath favor coatings of low porosity. A composite coating composed of nickel followed by copper with a nickel outer coat is said to have low porosity and to afford excellent protection.

Chromium Coatings.—A chromium surface upon exposure to air is immediately coated with a thin, invisible oxide coating which very effectively protects the metal from further attack. Such nontarnishing lustrous chromium coatings are widely used for their decorative value on bathroom fixtures, metal furniture, automobiles, hardware, radiator grilles, bumpers, and a host of other articles. Another important application of chromium coatings on gauges, machine parts, printing plates, rolls, etc., is due to its hardness and wear resistance. With the exception of the limited use of cementation (Chromizing), all chromium coatings are applied by electrodeposition. The common plating baths[1] contain chromic acid with small amounts of sulfuric acid, and are operated at slightly elevated temperature with insoluble anodes of lead, lead-antimony alloy, or steel.

In air and in most aerated aqueous solutions the passivating oxide film on chromium is quite permanent and is self-repairing if damaged. In the absence of oxygen and particularly in the presence of chlorides, the film on chromium is destroyed and the metal is liable to attack. In spite of the corrosion resistance of chromium, coatings of this metal do not give effective protection to a base metal because the commercial chromium coating invariably is porous and often contains a network of fine cracks. For this reason, chromium coatings on articles that are to be afforded corrosive protection are almost invariably placed on a bright nickel, or

[1] Haring and Barrows, *Nat. Bur. Standards Technical Paper* 346 (1927). Schneidewind, *Univ. Mich., Eng. Research Bull.* 8, (1927).

copper and nickel, undercoat. The undercoat provides corrosion protection to the base metal and the chromium coating maintains a bright, untarnished surface.

Copper Coatings.—Copper has moderately good resistance to corrosion in the atmosphere, in water, in salt solutions, and in alkaline solutions if sulfur compounds and ammonia are absent. It is also fairly resistant to nonoxidizing mineral acids and organic acids in the absence of oxidizing agents. Being cathodic to iron and most other commercial metals and alloys, it is not ordinarily recommended as a coating for protection against corrosion unless applied so as to give a completely nonporous coating, whereupon the corrosion characteristics of the article have become those of copper. Thin coatings find some use as underlying coatings to other metals and for other special uses.

Copper coatings of almost any desired thickness can be applied by electrodeposition from either acid copper sulphate or alkaline potassium cuprocyanide baths. Electroplated or sprayed copper coatings have found an important field of use in the selective carburization of steel, the parts to be protected from casehardening being covered with copper. Coatings are applied by cladding in the Copperweld process to form a composite wire which combines the high tensile strength of the steel core with the high electrical conductivity and corrosion resistance of the copper cladding.

Lead Coatings.—Lead is resistant to corrosion by the atmosphere, water, and most aqueous solutions due to the formation of a passivating oxide film which is self-healing in the presence of oxygen. It is one of the most resistant materials to industrial atmospheres containing sulfurous gases. It is rapidly attacked by strong alkalies and by some acids, particularly by organic acids such as acetic acid. Its resistance to sulfuric acid up to 80 per cent solutions, due to a film of lead sulfate, is notable and accounts for the use of much lead for lining chemical equipment.

Lead-coated sheet may be extensively deformed without damage to the coat; indeed lead coatings frequently are applied for the purpose of providing lubrication in drawing and stamping operations. Lead coatings also provide an excellent base for the application of paints. Being cathodic to iron, lead does not protect the base metal by galvanic action and a protective lead coating must be essentially free from pores. For this reason very thin lead coatings do not provide satisfactory protection to steel owing to the development of pinhole rusting.

Lead coatings may be applied by electrodeposition from either fluosilicate, fluoborate, or perchlorate baths; by spraying; or by hot dipping. Electrodeposited coatings are the most dense and sprayed coatings are the most porous. Slightly porous coatings may be improved by slightly rolling or burnishing the surface. In general, electrodeposited coatings 0.003 to 0.004 in. in thickness are relatively free from pores and afford good protection.

Homogeneous lead linings for iron, steel, wood, or brick supporting vessels are widely used in chemical plants. These linings may be attached to a steel base by nonmetallic fluxes or solders, or they may be applied by "burning" or welding on a layer of lead by directing an oxygen-hydrogen flame on bar lead.

It is practically impossible to apply satisfactory coatings of pure lead to iron or steel by hot dipping because iron and lead have no tendency to alloy and molten lead does not readily wet an iron surface. To form a bond, it is common practice to make use of a metal that will alloy with both lead and iron. Tin, antimony, cadmium, mercury, and zinc have been used for this purpose. Ordinary tin plate and galvanized sheet may be used as the base for producing lead-coated sheet by hot dipping. The bonding metal may be added to the lead bath as in the production of terneplate (lead-tin alloy) but the coating is then an alloy instead of relatively pure lead.

Aluminum Coatings.—Alloys of aluminum such as Duralumin may be successfully protected against attack in many environments by cladding the alloy with a thin coating of commercially pure aluminum (Alclad). Coatings of aluminum on steel applied by spraying, hot dipping, or cementation (Calorizing), are effective in preventing the scaling oxidation of ferrous metals at high temperatures. Aluminum coatings do not give the cathodic protection to ferrous materials that might be expected from its high position in the electromotive force series (page 414). In most environments, aluminum readily forms a very adherent oxide film which confers an apparent nobility on the metal.

Although aluminum alloys with iron, it is difficult to apply satisfactory coatings on ferrous materials by the usual hot-dipping procedures. Great care must be exercised to clean the iron surface and to keep the aluminum oxide content to a minimum. In a recent process, steel wire or sheet is degreased, pickled, passed through a flux of concentrated boric acid or borax after heating to 600°C. (1110°F.), heated in hydrogen at 800°C. (1470 to1830°F.),

and then passed into a molten aluminum bath under a hydrogen atmosphere.

Aluminum cannot be electrodeposited from aqueous solutions, but a method for its successful deposition from nonaqueous solutions[1] has now been reported.

Miscellaneous Metal Coatings.—Although the most important protective metallic coatings have been discussed, brief mention will be made of others of minor importance.

Cadmium coatings are anodic toward iron and steel and will therefore give galvanic protection to exposed base metal. The lower potential difference prevents cadmium from protecting as large an area of base metal as would be protected by zinc. The higher cost of cadmium coatings and other conclusive evidence that it is inferior to zinc for protecting ferrous materials in most environments have caused interest in cadmium coatings to wane in recent years. Its more pleasing appearance has led to its use in place of zinc for some applications in which it gives satisfactory protection. Most cadmium coatings are applied by electrodeposition from alkaline cadmium cyanide baths. However coatings of this metal may be applied by spraying and by hot dipping.

Cobalt coatings can be applied by electrodeposition but have little application. Coatings of tungsten, tantalum, vanadium, uranium, zirconium, and titanium can be applied to steel by cementation. The noble metals, silver, gold, and platinum, have long been applied as coatings for decorative and protective purposes in the production of jewelry, tableware, etc. Noble metal coatings also have found some industrial use as electrical contacts. The tarnish film that forms on silver has been shown to be silver sulfide and contains no oxide. Coatings of noble metals are almost always applied by electrodeposition.

Alloy Coatings.—For some applications, better appearance, corrosion resistance, or wear resistance can be obtained by coating a base metal with an alloy instead of a single metal. The possible combinations are almost infinite in number and only a few of the more important ones will be mentioned.

Brass coatings have been applied by the simultaneous electrodeposition of copper and zinc from alkaline cyanide baths since the early part of this century. By adjusting the bath composition, temperature, and current density, the composition of the brass can be carefully controlled. Thin brass coatings are widely used

[1] BLUE and MATHERS, *Trans. Electrochem. Soc.*, **69**, 529 (1936).

on iron and steel hardware and fixtures for decorative purposes, the coating usually being too thin and porous to give much corrosion protection. An intermediate thin coating of brass frequently is used between a base metal and an outer coating of nickel, chromium, or silver. Lately brass plating has come into rather wide use to secure satisfactory adhesion of rubber coatings to iron or steel. Brass coatings may be obtained by applying alternate layers of zinc and copper and then annealing the duplex deposit to obtain alloy formation.

In the "Coronite" process alloys of zinc and nickel, or zinc and tin of controlled composition, are deposited on iron or steel. These alloys may be applied by depositing the separate layers and then annealing. These coatings appear to afford superior corrosion resistance in many environments.

Cladding ordinary steel with stainless steel or with nickel-chromium alloys is a rapidly expanding industry, because these clad materials make the superior corrosion resistance and desirable appearance of these "stainless" alloys available at lower cost.

By a process almost identical with that used in the production of tin plate by hot dipping, an alloy coating of lead and tin can be applied. The product known as "terneplate" is widely used as "roofing tin" and for the production of gasoline tanks and other articles made by deep stamping operations. For the most common grade of terneplate made in this country, the coating consists of 75 per cent of lead and 25 per cent of tin.

Methods of Testing Metallic Coatings.—Space limitation prohibits a description of the standard methods that have been devised for testing metallic coatings, and the reader must consult the larger treatises.[1] In general the utility of a metallic coating will depend upon its uniformity, continuity, thickness, its electrochemical and physical relations to the basis metal, its adherence, the nature of the corrosion products which the coating metal forms in reacting with the environment, and probably a number of other factors. Naturally, the most satisfactory test is by actual long-time exposure to the actual environment. Frequently decisions must be made without the benefit of such information, and various short-time tests have been devised which will provide at least some basis for rendering judgment on the relative merits of various proposals.

[1] Burns and Schuh, *op. cit.*, pp. 234–274. "Symposium on Corrosion Testing Procedures," American Society for Testing Materials, Philadelphia (1937). The published standard tests of the A.S.T.M. should be consulted.

Nonmetallic Inorganic Coatings

There are a number of protective coatings for metals and alloys which are composed of nonmetallic inorganic substances. Some of these, such as the oxide coating produced by "anodizing" aluminum and its alloys, and vitreous enamels for iron and steel, are quite permanent protective coatings.

Vitreous or Porcelain Enamels.—Coatings of this type find wide application for ferrous materials used for equipment in the chemical, pharmaceutical, food, beverage, and dairy industries. Porcelain enamels are available that will withstand practically all chemicals except strong alkalies and hydrofluoric acid. Enameled steel also finds wide application on stoves, refrigerators, table tops, signs, the exterior of business and residential buildings, and kitchen utensils. Enameled cast iron is widely used for bathtubs and other sanitary ware.

The metal part to be enameled must be carefully cleaned of grease and oxide scale before the enamel is applied. The "frit" or glass for an enamel is made by fusing together refractory acidic substances, quartz and feldspar, with basic fluxes such as borax, fluorspar, cryolite, soda ash, sodium nitrate, and litharge. In the wet processes, the frit, which is very friable due to rapid quenching of the melt in water, is ground in a pebble mill with water, clay (floating agent), and the opacifier (usually tin, zirconium, or antimony oxide) or coloring agent. Exclusive of water, these mill additions rarely exceed 15 per cent of the weight of the frit. Prior to application of the mixture ("slip"), electrolytes such as soda ash or borax may be added to cause it to "set up" properly on the metal surface. The part to be enameled may be dipped in the slip or the slip may be sprayed on the metal. The coating, after drying, is fused or "burned" on in an enameling furnace. One to three coats may be applied in this manner. Almost invariably the ground coat contains cobalt oxide to promote adherence.

In the dry process, the frit is ground in a dry mill with opacifiers or coloring agents and the finely ground mixture is dusted onto the heated surface which previously has been given a ground coat by the wet process. The dusted-on coat is then fused in the enameling furnace.

The acid-resisting type of sheet-iron enamel contains higher proportions of silica and feldspar and lower amounts of the fluxes. Titanium dioxide is a common ingredient of these enamels. The

temperature and time employed for burning on an enamel coat depend upon the composition of the enamel and the proposed use of the enameled article. Cast-iron enameled by the wet process usually is fired at 625 to 760°C. (1150 to 1400°F.) for 10 to 15 min. Some enamels are fired at 700 to 870°C. (1450 to 1600°F.) for a period as short as 1 to 5 min. An enameled article cannot be appreciably deformed without injury to the coating.

"Anodized" Oxide Coatings on Aluminum.[1]—The protective oxide film that forms spontaneously on aluminum and aluminum alloys in air and in many aqueous environments has been mentioned previously. That a thicker, more protective, and stronger oxide film can be produced by making aluminum anode in suitable electrolytes has been known for many years. When properly prepared, the "anodized" coating provides high electrical insulation to the underlying metal, and possesses good resistance to corrosion and abrasion. The film may be colored with organic dyes and inorganic pigments to produce attractive decorative effects. The unidirectional current-carrying characteristics of the film have made possible the aluminum electrolytic condenser and rectifier.

The earlier processes for anodizing aluminum used electrolytes of chromic acid or of oxalic acid, but these have been replaced largely by the "Alumilite" process which employs sulfuric acid as an electrolyte. The latter process is more rapid, requires a lower voltage, and permits the production of films of a greater range of physical properties on aluminum and many aluminum alloys. The acid strength has been varied from 5 to 77 per cent and the temperature from 16 to 40°C. (60 to 105°F.) depending upon the characteristics desired in the film. To produce one of the standard uncolored coatings, the article is made anode in 15 to 18 per cent sulfuric acid for 30 min. at 22°C. (71°F.). A direct current of 13 amp. per sq. ft. is applied, requiring from 10 to 20 volts. After the anodizing treatment, the oxide coating is usually "sealed" by immersion in boiling water or in live steam for a time equal to that used in the electrolytic treatment. The sealing treatment partly converts the oxide to the monohydrate with an expansion in volume that decreases the porosity and increases the corrosion and stain resistance of the film. Sometimes to obtain still better corrosion resistance, treatment in dilute dichromate or sodium silicate solu-

[1] BURNS and SCHUH, *op. cit.*, pp. 368–373. EDWARDS and KELLER, *Trans Electrochem. Soc.*, **79**, 135 (1941).

tions at 80°C. (176°F.) is substituted for the hot-water sealing operation.

If colored coatings are to be produced, the anodizing is carried out in higher acid concentrations and at higher temperatures to obtain a more porous coating. The anodized articles are then immersed in a solution of a dye, or an inorganic pigment is precipitated in the film, before the sealing operation. For protection against corrosion, a film thickness of about 0.004 in. is used. In the various applications film thickness will range from 0.0001 to 0.001 in.

The oldest and perhaps most general application is in the protection of aluminum and aluminum alloys used in aircraft construction. These anodized coatings also are applied to aluminum and its alloys used in window frames, refrigerator ice trays, machine parts, pistons, reflectors, etc. In many applications the hardness, abrasion resistance, and low coefficient of friction of the anodized coating are important.

Surface Conversion or Chemical-dip Coatings.—These coatings are produced by covering the surface of a metal or alloy, by immersion or by spraying, with a solution of a chemical which will react with the metal surface to produce an adherent coating of metal compound that is practically insoluble in the intended environment. In general these coatings are not especially permanent, but they may afford good protection in some environments and during storage. Furthermore, many of these coatings serve as excellent bases for the application of paints and other organic protective coatings.

The corrosion resistance of zinc, zinc coatings, and zinc-base die castings may be increased by immersion in sodium dichromate solutions acidified with dilute sulfuric acid ("Cronak" process) or by the application of a phosphate coating. Magnesium and magnesium alloys (Dowmetal) are afforded better protection in ordinary atmospheres by painting if the surface is given a preliminary treatment for 0.5 to 2.0 min. in a solution containing 1.5 lb of sodium dichromate and 1.5 lb. of concentrated nitric acid per gallon. An alternative treatment for magnesium alloys consists of a 30-min. anodic treatment in a sodium dichromate-sodium phosphate bath.

A smooth gray coating may be placed on aluminum by immersion for 5 to 10 min. in a boiling solution containing 20 g. of sodium carbonate and 5 g. of potassium dichromate per liter.

Various surface conversion coatings have been applied to iron and steel to prevent rusting in ordinary atmospheres and to serve as bases for subsequent paint coatings. Coslett treated iron surfaces with a solution of phosphoric acid and ferrous sulfate or zinc sulfate as early as 1908. In 1918, Parker found that the character of the phosphate coating was improved by using a solution of primary manganous phosphate ("Parkerizing") with some added manganese dioxide. In 1929, the Parker process was improved to require less time by using solutions of manganese dihydrogen phosphate containing a small amount of a copper salt ("Bonderite A"). A further improvement in the process ("Spra Bonderite") has reduced the processing time to from 30 to 60 sec. In this treatment the steel is sprayed with a dilute alkaline solution, rinsed with water, and then sprayed with a solution of chromic acid and sodium chloride. A very similar solution is used in a treatment known as "Chromodizing." In the "Laxal" treatment for steel, solutions of oxalic acid are used. An oxide coating is produced on steel in the "Bower-Barff" process. The steel, after cleaning, is heated to 650°C. (1200°F.) for about seven hours in a closed retort in which air is displaced with steam at about 100 lb. pressure, or a mixture of steam and benzene. After this treatment, the steel is cooled to 150°C. (300°F.), dipped into hot boiled linseed oil, and held at this temperature until the oil is oxidized.

It is possible artificially to produce a green "patina" on copper which is similar to the protective coating that develops when copper is exposed to the atmosphere. The natural patina consists mainly of basic copper sulfate. Satisfactory artificial patinas have been developed by painting or spraying copper twice daily for a week with a 10 per cent solution of ammonium sulfate, followed by two days' of treatment with a 10 per cent solution of copper sulfate to which 1 per cent of sodium hydroxide or other alkaline hydroxide or carbonate has been added. Sometimes ammonium nitrate (5 per cent) is added to the copper sulfate solution. During treatment the copper is exposed to the air, but it is protected from the sun in hot weather.

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CHAPTER XI

BUILDING STONES

By Thomas R. Alexander, Ph.D.

Although practically all rocks are suitable for building construction from the point of view of their mechanical strength, there are other requirements that they may not be able to meet, and that may cause the stone to be rejected as unfit for building purposes. Among the important properties that must be taken into account are the durability of the stone, its tendency to discolor, and its resistance to the effects of fires. There are three main classes of rocks: igneous rocks, sedimentary rocks, and metamorphic rocks. Each class includes a large number of members that differ widely from one another in composition and structure. Only a few of the many varieties of rock are suitable and available for use as building stone.

Igneous Rocks

Igneous rocks were formed by the solidification of molten material as it was forced up into or through outer layers of rock. In most cases this fused material solidified before it reached the surface, and is called plutonic rock. If it came to the surface before solidification, it is called volcanic rock.

Structure.—Igneous rocks are divided into two classes on the basis of structure. Those that solidified quietly from a state of fusion and were not later subjected to severe external stresses are made up of crystals irregularly arranged and are called *massive* igneous rocks. Slow cooling produced a coarse-grained rock and rapid cooling a fine-grained one. Igneous rock that has been subjected to very great pressure has a banded structure. In some cases the constituent minerals are found in more or less definite alternating bands; in other cases they are merely arranged with their long axes in the same direction. In either case the rock is called a *gneiss*.

Chemical Composition.—The igneous rocks range from 36 to 80 per cent of silica with alumina as the second most abundant

constituent. The following is an average by F. W. Clarke from the analyses of 830 American igneous rocks.[1]

Constituent		Per cent
Silica	SiO_2	59.71
Alumina	Al_2O_3	16.01
Ferric oxide	Fe_2O_3	2.63
Ferrous oxide	FeO	3.52
Lime	CaO	4.90
Magnesia	MgO	4.36
Potash	K_2O	2.80
Soda	Na_2O	3.55
Water	H_2O	1.52

Acid igneous rocks are those which are high in silica and low in lime, magnesia, and iron oxides. Basic igneous rocks are high in basic oxides and low in silica.

Commercial Classification.[2]—Quarrymen and builders have adopted the following simple classification: (1) granites, (2) traps, and (3) serpentines.

Granites.—The granites are crystalline, plutonic rocks composed largely of quartz and feldspar, usually with some mica and occasionally hornblende. They are acid rocks.

Quartz, SiO_2, is the hardest of all the common minerals. Its crystals vary in luster and color, depending on the impurities in them. It is extremely resistant to weathering.

Feldspar is essentially a silicate of aluminum combined with the oxide of another metal. Its color also depends on the impurities that it contains. The common or potash feldspar has the composition indicated by the formula $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$. Albite or soda feldspar is usually found in granites. It weathers easily and is converted into clay (see Chap. XIV).

Mica in granite may be of two kinds: either the white, called muscovite, or the black, known as biotite. The composition of the former corresponds to the formula $H_2KAl_3(SiO_4)_3$ and the latter to the formula[3] $(H,K)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3$. Mica occurs

[1] Quoted from Eckel, "Building Stones and Clays," p. 23, John Wiley & Sons, Inc., New York (1912).

[2] Eckel, *op. cit.*, p. 30.

[3] Symbols in parenthesis, separated by commas, indicate variability in composition.

in granite in the form of smooth, shining scales which cleave readily into thin, elastic leaves. It weathers easily, but unless present in large quantities it is not injurious.

Hornblende is a complex silicate of calcium, iron, magnesium, and aluminum. Its color is usually dark green to black, and it is more resistant to weathering than mica.

Good granites are usually either gray or reddish, since granites of these colors are composed of minerals that are more resistant to weathering. The black or greenish granites are less durable. On weathering the color changes to a yellowish shade.

Trap Rock.—The name of this rock is derived from the Swedish word *trapp*, meaning stairs; the term has reference to the appearance of the rock in the quarry. Trap rock consists mainly of soda or lime feldspar and hornblende. It is a basic rock, fine grained, compact, and dense; it may occur either in the massive or gneiss formation. It is usually dark in color and, like all basic rock, weathers considerably.

Trap rock is stronger and more dense than granite, but this advantage is more than offset by the fact that the stone is very tough and that it splits irregularly. These properties, which limit its use as a building stone, make it very useful stone for paving blocks, curbs, railway ballast, and concrete aggregates.

Serpentines.—These are generally of igneous origin but not directly so. They have been produced by the action of water, or of water and carbon dioxide on basic igneous rock and are, therefore, metamorphic rocks.[1] A typical reaction is $2Mg_2SiO_4 + CO_2 + 2H_2O = H_4Mg_3Si_2O_9 + MgCO_3$. This equation represents the conversion of olivine into pure serpentine. The rock has a soapy feel and is soft enough to be easily cut with a knife. It is not much used as a building stone, since in most deposits the rock is irregularly jointed and large blocks are difficult to obtain. It is unsuitable for exterior use because it is not sufficiently resistant to weathering influences. Under the trade name of "Alberine" stone it is used extensively for sinks, washtubs, laboratory table tops, and similar articles.

Sedimentary Rocks

Sedimentary rocks are those that have been formed by the solidification of material resulting from the disintegration of other

[1] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, p. 421, Longmans, Green and Company, New York (1925).

strata. The substances involved are mainly clays, sand, and calcium carbonate which have been carried by and deposited from water. Marine organisms that secrete calcium carbonate and silica in their shells and bony structures have also contributed largely to the accumulation of this type of rock. Since these rocks were formed from sediments, they consist of layers of different composition, color, structure, etc., depending upon conditions prevailing at the time of deposition. Sedimentary rocks split more easily along the bedding planes than in other directions; because of this they are less suitable than igneous rocks for use in massive structures. They should never be set in a wall on edge, since thin layers may split or scale off where exposed to the weather. Sedimentary rocks considered in this discussion will be taken up in the following order: slates, sandstones, limestones, and marbles.

Slates.—Slates are the hardened, more or less metamorphosed, siliceous clays that collected as sediment on ancient sea bottoms.[1] The intense pressure to which the material was subjected caused it to expand at right angles to the directions of the pressure; as a result, the crystals of mica and chlorite have their flat surfaces parallel. This gives to slate its characteristic tendency to split with ease in one direction—a property known as "slatey cleavage."

Composition.—Since slates are derived from clayey rocks, they consist essentially of the silicates of aluminum, calcium, magnesium, potassium, and sodium. The range of chemical composition of average slate is given by Bowles.[2]

RANGE OF CHEMICAL COMPOSITION OF SLATE,* PER CENT

Silica	SiO_2	50–67
Alumina	Al_2O_3	11–23
Ferric oxide	Fe_2O_3	0.5–7
Ferrous oxide	FeO	0.5–9
Potash	K_2O	1.5–5.5
Soda	Na_2O	0.5–4
Magnesia	MgO	0.5–5
Lime	CaO	0.3–5
Water	H_2O	2.5–4

* Less important constituents omitted.

The chief mineral constituents of slate are: mica, 38 to 40 per cent; quartz, 31 to 45 per cent; and chlorite, 6 to 18 per cent.

[1] BOWLES, "The Stone Industries," 2d ed., Chap. X, McGraw-Hill Book Company, Inc., New York (1934).

[2] BOWLES, *op. cit.*, p. 231.

Color.—The color of roofing slate is of great importance. The most common color is some shade of gray or bluish gray; less common varieties are black, green, or purple. In most cases these colors are dependent upon the amount and condition of two ingredients: organic matter and oxides of iron. If the slate contains considerable finely divided carbonaceous matter, it will probably have a glossy black color; if it is high in ferric iron, it will probably be red or purple; if high in ferrous iron, it may be green unless this color is masked by black carbonaceous matter. The glossy black slates are usually finer and more evenly grained, softer, and smoother than slates of other colors. The gray slates are coarser in grain and much harder.

Discoloration of Slates.—Discoloration is due to the atmospheric oxidation of ferrous carbonate: $2FeCO_3 + 3H_2O + \frac{1}{2}O_2 = 2Fe(OH)_3 + 2CO_2$. If other colors are well masked by the black material, discoloration may not be great; but since the amount of ferrous carbonate often varies in the different beds of the same quarry, it may happen that patches of slate on the same roof will fade while others do not.

Sandstones.—These rocks are made up essentially of grains of quartz bound together by some cementing material, which may be silica, iron oxide, calcium carbonate, or clay. Upon this basis sandstones are divided in the same order into siliceous, ferruginous, calcareous, and argillaceous stones, although more than one kind of cementing material is often found in the same stone. Mica, pyrite, and other minerals are also found in sandstones. The color, strength, and durability of the stone depend in large measure on the nature and amount of cementing material.

Colors.—The red and reddish-brown colors are due to the presence of ferric oxide; the yellow and yellowish-brown to the presence of the same oxide in the hydrated condition. Bluish to greenish tints may be due to iron sulfide, ferrous carbonate, or ferrous silicate. Carbonaceous material may give the stone a gray or black color.

Durability.—This property of sandstones varies considerably. Stones with clay seams are liable to split with repeated thawing and freezing. Those containing mica scales along the bedding planes are liable to flake off, especially if the stone is set in a wall on edge.

Of all varieties, the siliceous sandstone is most resistant to the action of the weather. If the stone is composed of silica alone, it is frequently so hard that it is difficult to dress.

The ferruginous sandstones stand second in respect to durability. The "brownstones" of the eastern states are generally sandstones of this sort. They are of granitic origin and usually contain feldspar and mica in addition to the quartz and iron oxide. They are easy to dress, but less durable than the siliceous stones.

The calcareous sandstones are generally light colored or gray and, although strong, are soft and easily worked. Because the cementing material, calcium carbonate, is leached out by the action of carbon dioxide and water, they do not resist the action of the atmosphere well. The argillaceous sandstones are the least durable of all. They absorb water readily, hence they are particularly susceptible to the action of frost. Being comparatively soft, they are easily dressed. Some sandstones have little if any cementing material, but owe their strength to the pressure to which they were subjected during formation. Certain varieties of such sandstone, whose grain size is small and uniform, are used in the manufacture of grindstones and whetstones. They wear away with use, always presenting fresh, sharp surfaces. Occasionally they are sufficiently coherent to be used as building stones.

All sandstones, when freshly quarried, contain a certain amount of water which renders them very susceptible to injury if allowed to freeze. As the stone dries it becomes harder, due to the fact that cementing material which was dissolved in the water is left behind on evaporation.

Limestones.—Limestones are stratified rocks that consist essentially of calcium carbonate. They have been produced largely from deep-sea deposits of the calcareous remains of animal organisms, whose shell formations are often distinguishable in the rock. The particles are cemented together by calcium carbonate that has been deposited from solution. Pure calcium carbonate in mineral form is known as *calcite.* Limestone contains varying amounts of other substances such as iron oxide, silica, clay, and carbonaceous material. As the amount of silica increases, limestone merges into calcareous sandstone; with a different quantity of clay it becomes a calcareous shale. Magnesium carbonate is usually present in limestone. If equimolecular proportions of the two carbonates, $CaCO_3 \cdot MgCO_3$ are present, the mineral is called *dolomite.* Pure magnesium carbonate is called *magnesite.* The term limestone is usually restricted to those rocks that contain less magnesium carbonate than dolomite. Those that contain more are impure magnesites.

Limestones may be white, gray, blue, or black, depending on the impurities present. Both limestones and dolomites are moderately durable, though less so than good sandstone or granite.

Marbles.—In accordance with strict geologic definition, marbles are those highly crystalline formations that have been developed from limestones or dolomites by heat and pressure; they are, therefore, metamorphic rocks. The original limestone or dolomite was converted into a semifluid mass by intense heat and under high pressure which prevented the escape of carbon dioxide; during cooling, it crystallized.

Commercially the term marble has a much broader meaning. It includes any limestone, crystalline or not, which is capable of taking a high polish and which, when polished, will have a pleasing appearance. Even serpentine rocks which can be used as marble substitutes are classed as marble, though they contain little calcium or magnesium carbonate. Marbles may be divided into three groups:[1]

1. Highly crystalline marbles resulting from the recrystallization of limestone. Usually white or with gray, black, or other markings. This is the largest group.
2. Subcrystalline or fossiliferous marbles in which crystalline structure is rarely noticeable, the value depending rather on color effects than on texture.
3. Onyx marbles. Translucent rocks showing color banding, due to the fact that they were formed layer after layer by chemical deposition from cave or spring waters.

Marble does not differ from limestone in chemical composition and is likely to contain the same impurities, some of which are objectionable. Mica, if abundant and present in bands or patches, interferes with the polishing of the stone; weathering may also leave a pitted surface. Iron pyrite is quite objectionable because weathering converts it into a red basic ferric sulfate and sulfuric acid. The latter, of course, attacks the stone.

Color.—Marbles show a wide variation in color. Some are white, others vary from gray to black; red, pink, yellow, green, or brown marbles are frequently used. The gray and black coloring matter is carbonaceous (usually fine scales of graphite); the red, pink, and brown colors are due to oxides of iron and manganese. The coloring matter may be uniformly distributed or it may be segregated, giving the marble a mottled appearance.

[1] Eckel, *op. cit.*, p. 166.

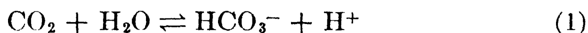
Some ornamental marbles show what is termed a brecciated structure. These marbles are made up of angular pieces of crushed rock, with the spaces between filled with mineral matter that was deposited later.

Durability.—The weather-resisting ability of marble is about equal to that of limestone. Those that contain much mica and those with a brecciated structure are less durable.

Deterioration of Stone.[1]—Deterioration of stone may be due to either physical or chemical causes, or to a combination of the two. The agencies may be purely external, or their effects may be supplemented by changes within the rock itself.

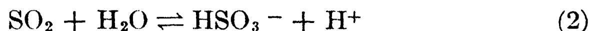
Chemical Reactions.—The ingredients of practically all building stones are nearly insoluble in pure water, but rain water is never pure. It contains dissolved oxygen and carbon dioxide from the air; after it comes in contact with the grime and soot on buildings, it will have various other compounds dissolved in it, including both sulfurous and sulfuric acid in small amounts. These latter impurities are due to the presence of sulfur dioxide in the atmosphere and are much more important in industrial areas where bituminous coal is being burned in large quantity.

When carbon dioxide dissolves in water, the two react.



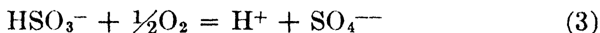
$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad (1)$$

Sulfur dioxide reacts in the same way.



$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+ \qquad (2)$$

Both solutions are weakly acidic, but the sulfurous acid reacts with dissolved oxygen as follows:



$$HSO_3^- + \tfrac{1}{2}O_2 = H^+ + SO_4^{--} \qquad (3)$$

Since sulfuric acid is a much more active acid than sulfurous, the acidity of the solutions is greatly increased. The carbonate rocks or other rocks, such as calcareous sandstones, are attacked by water which is even mildly acidic. The equation for the reaction is $CaCO_3 + H^+ \rightleftharpoons Ca^{++} + HCO_3^-$. Since the calcium carbonate is soluble in water, the products of the reaction will be washed away from the surface of the stone. Magnesium carbonate is similarly changed, as are mortars and cements that contain free

[1] For a more complete discussion with bibliography see Bowles, *op. cit.*, Chap. XV.

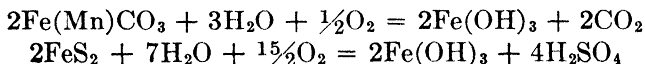
lime. Feldspar, hornblende, and even silica in such rocks as granites, sandstones, and slates react with water that contains acids, but the reaction is much slower. The conversion of feldspar into clay is usually represented as being due to the following reaction:



$$K_2Al_2Si_6O_{16} + 2H_2O + CO_2 = Al_2Si_2O_7 \cdot 2H_2O + K_2CO_3 + 4SiO_2.$$

Sulfuric acid converts calcium and magnesium carbonates into sulfates which are rather easily removed from stone surfaces. When, on the other hand, the water in which these two salts are dissolved is retained in the pores of the stone, it will evaporate slowly and crystals of gypsum, $CaSO_4 \cdot 2H_2O$, and Epsom salt, $MgSO_4 \cdot 7H_2O$, will separate. The volumes occupied by these two salts are considerably greater than those of the carbonates from which they were derived, and internal strains are set up which may be serious. The more porous stones suffer greater deterioration from this cause.

Oxidation.—Changes in the color of stones are frequently due to oxidation. Oxidizable materials frequently met with are ferrous carbonate, manganous carbonate, sulfides of iron (pyrite and marcasite), and silicates of the same metals. The reactions cannot be described in simple equations; the ones used indicate merely the type of reaction that may be involved.



$$2Fe(Mn)CO_3 + 3H_2O + \tfrac{1}{2}O_2 = 2Fe(OH)_3 + 2CO_2$$
$$2FeS_2 + 7H_2O + \tfrac{15}{2}O_2 = 2Fe(OH)_3 + 4H_2SO_4$$

Structural damage, if any, may result from the sulfuric acid, which can produce the secondary effects noted above. Sea water, river water, and even ground water may cause deterioration in stone.

Physical Agencies.—Repeated temperature changes, especially through a considerable range, have a weakening effect on stone. Alternate and unequal contraction and expansion of the various substances in the stone produce strains which are enhanced by the fact that rock is a poor conductor of heat, thus subjecting the surface and the interior to different strains. The more complex rocks, such as granite, suffer greater deterioration from this cause than do the simpler carbonate rocks.

The effect of freezing on sandstones that still contain their "quarry water" has been mentioned. If the pore space is not too completely filled, freezing will not damage the stone, and

stone from which the quarry water has been removed will not reabsorb enough water from its exposed face to make freezing dangerous. If, however, the stone should be seamed, water may collect and the stone be damaged by freezing.

Fire Resistance.—No stone can withstand the extreme heat developed by the burning of large buildings. Granites seem to be the least resistant and sandstones the most. Limestones show good resistance at temperatures below 600°C., but at about this point the stone decomposes appreciably into carbon dioxide and lime.

Preservation of Stone.—The use of protective coating materials on stone surfaces is not likely to be of great interest. Some study of the subject has been made, using water-proofing compounds in volatile solvents.

Cleaning of Stone.—Methods of cleaning are (1) the mechanical removal of the old surface, usually done by sand blasting, wire brushing, grinding, or heating with a blowtorch; (2) scrubbing

TABLE 74.—PRODUCTION OF BUILDING STONE IN THE UNITED STATES (1939)

Rough

	Construction		Architectural	
	Cu. ft.	Value	Cu. ft.	Value
Granite	2,241,800	$ 410,395	273,140	$ 253,537
Basalt	127,910	14,619		
Marble	....	....	313,270	664,998
Limestone	3,872,640	424,230	3,367,550	1,426,020
Sandstone	836,130	190,940	291,110	360,572
Miscellaneous	601,880	654,342		
Total	7,680,360	$1,694,526	4,245,070	$2,705,127

Finished

	Sawed		Cut	
	Cu. ft.	Value	Cu. ft.	Value
Granite	297,470	$ 932.540	294,520	$1,479,128
Marble	232,040	464,900	501,520	3,574,149
Limestone	1,430,700	925,250	2,059,130	3,627,180
Sandstone	121,000	153,332	118,850	452,153
Total	2,081,210	$2,476,022	2,974,020	$9,132,610

with water and various cleaning agents such as soap or caustic soda. These cleaning materials and others must be completely removed from the stone surface or they may damage it. Acids, especially hydrochloric and hydrofluoric, are effective but they may discolor the stone.

The amounts and kinds of building stone sold or used by producers in the United States in 1939 are given in Table 74.[1]

References

BOWLES: "The Stone Industries," 2d ed., McGraw-Hill Book Company, Inc., New York (1934).

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[1] BOWLES and JENSEN, "Minerals Yearbook," 1940, p. 1166, U.S. Department of the Interior.

CHAPTER XII

LIME AND GYPSUM PRODUCTS

By Thomas R. Alexander, Ph.D.

Lime, or quicklime as it is sometimes called, is essentially calcium oxide, CaO, although the term is also applied to mixtures in which calcium oxide is the principal ingredient. Pure calcium oxide is a white solid which melts at 2570°C. (4660°F.). When the molten material is cooled, it solidifies in cubic crystals, but as ordinarily prepared it is noncrystalline, easily powdered, and has a specific gravity varying from 3.08 to 3.30. The specific gravity of lime depends on the temperature to which it has been heated, higher temperatures giving a more dense product. As a consequence of the decrease in the ratio of surface to mass which accompanies increase in density, the chemical reactivity of lime decreases as the density increases. The reaction between lime and water, which is known as "slaking," produces calcium hydroxide:



$$CaO + H_2O = Ca(OH)_2 + \text{heat.}$$

The reaction is quite rapid when the lime is not in the compact or crystalline state and, since heat is evolved rapidly, high temperatures will result unless care is taken to provide for the escape of heat or to control the speed of the reaction by regulating the conditions of mixing.

Calcium hydroxide produced by the slaking of lime is an amorphous white powder, slightly soluble in water, from which it separates in crystalline form during slow evaporation. If heated to about 400°C. (750°F.), calcium hydroxide decomposes into the oxide and water.

Limestone.—Lime is produced by heating limestone, which is more or less pure calcium carbonate as indicated by the range of composition of a representative group of limestones in Table 75. During the heating, carbon dioxide is driven off and nonvolatile impurities such as the oxides of silicon, magnesium, aluminum, iron, and manganese are left behind in the lime. Limestone is a sedimentary rock (see Chap. XI) which frequently contains

considerable clay that has been deposited with it. The heating of this material produces calcium silicates and aluminates (see Chap. XIII) with correspondingly less free lime. When the proportions of silica and alumina are high enough, natural cements are produced. Since quicklime for structural purposes should not contain more than 5 per cent of silica, alumina, and iron oxide combined, the limestone used must be correspondingly lower in these oxides.

TABLE 75.—COMPOSITION OF LIMESTONE*

	Per Cent
Total carbonates	97
CaO	29.77–55.56
MgO	0.31–21.23
SiO_2	0.14–2.41
$Al_2O_3 + Fe_2O_3$	0.5

* PORTER, "Manufacture of Lime," p. 7, *Nat. Bur. Standards, Circ.* 337.

Dolomitic Limestone.—Most limestones contain some magnesium carbonate. When the two carbonates are in equimolar proportions, $MgCO_3 \cdot CaCO_3$, the mineral is called *dolomite;* limestones that contain smaller amounts of magnesium carbonate are usually referred to as *dolomitic limestones.*

Magnesium carbonate decomposes when heated into magnesium oxide, MgO, and carbon dioxide. The temperature required is considerably lower than that required to decompose calcium carbonate, hence dolomitic limestone will produce a mixture of lime and magnesia when burned. Magnesium oxide reacts with water slowly if it has not been heated to too high a temperature. The hydroxide that results is decomposed at a lower temperature than that required to decompose calcium hydroxide; it is less soluble in water and in the solid state it reacts only slightly with carbon dioxide.

Uses of Lime.—Table 76 gives a summary of the more important uses of lime, along with tonnage and price data for the year 1939.

Manufacture of Lime.[1]—Limestone is burned in kilns which may be either vertical shafts or rotating kilns similar to those used in Portland cement manufacture, and operated in much the same way. In some vertical-shaft kilns, coal and limestone are fed into the top in alternate layers. Lime is removed periodically

[1] AZBE, "Symposium on Lime," p. 88, American Society for Testing Materials, Philadelphia (1939).

TABLE 76.—USES OF LIME*

Use	Percentage of total	Short tons	Total value	Average price per ton
Agriculture	8.5	362,335	$ 2,214,759	$6.11
Building	23.5	1,000,498	8,563,792	8.56
Glass	3.5	148,102	1,003,843	6.78
Metallurgy	17.6	748,853	4,328,564	5.78
Paper	10.9	464,224	2,904,160	6.26
Sugar refining	0.4	18,831	167,480	8.89
Tanning	1.7	70,446	475,841	6.75
Water purification	5.9	251,193	1,594,214	6.35
Other uses*	12.2	518,305	3,349,187	6.46
Total	84.2	3,582,787	$24,601,840	

* MOYER and COONS, "Minerals Yearbook," 1940, p. 1245, U.S. Department of the Interior.

from the bottom of the shaft while the charge is continuously introduced at the top. In other vertical-shaft kilns, fuel is burned in a fire-box at the bottom of the shaft so that the heat passes up over the charge, but the lime does not come in contact with the ashes. The temperature in the hottest part of the kiln is usually between 900 and 1200°C. (1650 and 2190°F.). The charge must be kept at the required temperature long enough to decompose it throughout and the carbon dioxide must be removed to prevent recombination. The time required depends on the chemical and physical characters of the stone. A stone that is high in magnesium carbonate will burn more quickly than a purer calcium carbonate; one that is compact will conduct heat more rapidly than a porous one and therefore burn more rapidly. Since the loss of porosity (increase in density) previously mentioned takes place slowly even at the minimum temperature required in the kiln, the charge should not be allowed to remain in the kiln longer than necessary.

Structural Lime.—The composition and the properties of lime depend on the composition of the limestone and the temperature at which it has been burned. Limestone burned at the minimum temperature produces a porous or "soft" lime whose volume may not be much less than that of the original stone in spite of the elimination of the carbon dioxide. Higher temperatures produce a more compact lime, usually called "hard" lime. Quicklime that is to be used for building purposes after slaking should have the following composition:

TABLE 77.—COMPOSITION OF BUILDING LIME*

	Calcium lime	Magnesium lime
CaO (min. %)	75	
MgO (min. %)	. .	20
CaO + MgO (min. %)	95	95
$SiO_2 + Al_2O_3 + Fe_2O_3$ (max. %)	5	5

* A.S.T.M. Standards (1939), Part II, p. 30.

High-calcium lime slakes more rapidly than magnesium lime and, when used in mortar, develops a higher early strength, although the magnesium lime surpasses the calcium lime somewhat in ultimate strength.

Slaking of Lime.—The reactions involved in this operation have been discussed briefly. The object of the slaking operation is to prepare a smooth paste of calcium hydroxide (hydrated lime), and the operation was formerly carried out by laborers at the place where the lime was to be used. Results were not always satisfactory, since the heat developed was not carried away rapidly enough to prevent the cores of the larger lumps from being overheated. This produced grains of lime that slaked slowly; when these grains were incorporated in the mortar, the continued slaking, with consequent increase in bulk, caused faults to develop.

Hydrated Lime.—The inefficiency of the older method of slaking lime has led to the manufacture and use of hydrated lime. Quicklime in lumps not more than 1 in. in diameter is treated with just enough water to combine with the free lime. The resulting powder is sieved and the coarse particles of unburned limestone, overburned lime, silicates, etc., removed. Although the product combines readily with carbon dioxide, the surface crust of carbonate protects the well-packed material from contact with the air, so that it can be stored and handled without serious deterioration.

Hydraulic Limes and Grappier Cement.—Limestones that contain too much silica, alumina, and iron oxide to make a satisfactory quicklime can be calcined at somewhat higher temperatures to produce a product known as hydraulic lime. Material of this kind will slake in contact with water, due to the presence of free lime. Continued contact with water causes the hydration of the aluminates and silicates that are also present, and the mass solidifies. The slaking of the lime takes place first and, if a limited amount

of water is used, the core of unattacked calcium aluminates and silicates may be removed from the powdered calcium hydroxide by screening. The coarse particles are collected, ground, and sold as Grappier cement. It is used for stuccowork and in laying marble and other stone that would be stained by ordinary Portland cement. The setting process resembles that of Portland cement (Chap. XIII).

Lime-sand Mortar.—Lime paste alone is not suitable for use as a mortar. If the paste is allowed to dry, it shrinks greatly and cracks. In practice, sand is always added to it; the proportions are about 2½ or 3 of sand to 1 of paste. The addition of this inert material almost eliminates shrinking and prevents cracking. Also, the addition of sand makes the mass more porous, so that the penetration of the carbon dioxide necessary for the hardening of the mortar is facilitated. It is important that the sand and paste should be mixed in about the proportions indicated, since with these amounts the paste will just fill the voids between the sand grains. If much more sand than this is used, the mortar will be weak because it will be too porous. If less is used, the resultant excess of paste will cause a shrinkage when drying. It is better to have too much rather than too little sand; a slight sacrifice of strength is immaterial, but shrinkage will cause cracks that are immediately noticeable. If sands of different degrees of coarseness are mixed, the voids between the sand grains will be lessened and a smaller proportion of paste may be used without the mortar's becoming too porous. The working qualities also are affected by the amount of sand. If too much sand is used, the mortar will be "short"; if too little, it will be sticky.

The effect of impurities in lime that is to be used for mortar is considerable. Silica reduces the plasticity and the sand-carrying capacity of the lime, but does not change the hardness or strength of the mortar. Iron oxide affects plasticity and the sand-carrying capacity in the same way, but higher percentages actually increase the strength and hardness. Small amounts of alumina improve the lime; gypsum is detrimental.

Hardening of Lime-sand Mortar.—Compared to the hardening of Portland cement, the hardening of lime-sand mortar is a very simple process. The initial "set" is due to the evaporation of the water. If used with porous bricks, it may set very quickly because much of the water is taken up by the bricks. Contact with the air results in reaction between the lime and carbon dioxide forming

an interwoven mass of calcium carbonate crystals which are responsible for the strength of the mortar. Contact between the lime and carbon dioxide is confined to the exposed surface of the mortar due to the fact that the crystalline layer prevents diffusion of gases into the interior of the mortar; therefore the interior of the hardened mortar always contains free lime.

Lime-sand Brick.—Brick sufficiently strong for many structural purposes is made by mixing sand with about 10 per cent of its weight of slaked lime, compressing in molds, and then heating in an autoclave with steam at pressures ranging from 5 to 10 atm. for several hours. The hardening process is due to the formation of calcium silicates.

Gypsum Products

Gypsum.—The mineral gypsum, from which various kinds of commercial plasters are prepared, is the hydrated calcium sulfate $CaSO_4 \cdot 2H_2O$. It frequently occurs in the massive form known as *rock gypsum*, or it may be found as a granular variety known as *gypsum sand*. It sometimes occurs in a relatively pure state, but usually it contains small amounts of impurities such as silica, alumina, iron oxide, and the carbonates of calcium and magnesium. An earthy variety known as *gypsum earth* or *gypsite* may contain 50 per cent or more of such impurities, especially silica and the carbonates mentioned. Pure gypsum is white and, when crystalline, it is more or less translucent. It is so soft that it can be readily scratched with the thumbnail. *Alabaster* is a pure variety of gypsum which is used to some extent for statuary. A crystalline variety, practically colorless and transparent, is known as *selenite*. The selenite crystals are frequently laminated, splitting into thin leaves like mica but, unlike mica, the leaves are inelastic.

Preparation of Gypsum Plasters.—The manufacture of gypsum plasters from native gypsum is based on a process of dehydration. As described by Stone,[1] when the dihydrate is stirred and heated with gradually increasing temperature, the water of crystallization begins to be evolved rapidly at about 110°C. (230°F.). The escape of the resulting steam causes an appearance of boiling in the powdered mass. This agitation continues until a temperature of about 130°C. (266°F.) is reached, when the boiling largely

[1] "Gypsum Products," *U.S. Bur. Mines Tech. Paper* 155, p. 17 (1917). Lea and Desch, "The Chemistry of Cement and Concrete," p. 17, Edward Arnold & Co., London (1935).

ceases and the mass settles down to about 86 to 90 per cent of its original volume. This quiet stage is called the first settle and indicates that most of the dihydrate has been converted into the hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$.

If the heating is continued beyond this point, the dehydration is resumed and a second boiling, more vigorous than the first, is noted. When the mass quiets down again, the second settle is said to have been reached. At this stage all of the dihydrate has been converted into the hemihydrate, and some of it has been completely dehydrated to form the soluble anhydrite. This degree of dehydration reduces the bulk of the mass to about 82 to 85 per cent of the original volume of the gypsum.

Depending upon the variety of plaster desired, dehydration is discontinued either before or after the second settle. In making wall plaster, for example, it is common practice to stop the calcination after the first settle at temperatures ranging from 155 to 175°C. (310 to 350°F.). Depending upon the extent of the calcination, plaster of Paris, which is commonly called stucco in the trade, is spoken of as first- or second-settle stucco.

Setting and Hardening of Gypsum Plasters.—The setting of the gypsum plasters depends upon the fact that the hemihydrate and the soluble form of anhydrite are more soluble in water than the dihydrate. The hemihydrate dissolves and combines with water to form the dihydrate, which precipitates from the solution as a solid mass of fine, interlaced crystals. The equation for the hydration may be written as follows:



$$CaSO_4 \cdot \frac{1}{2}H_2O + 1\frac{1}{2}H_2O = CaSO_4 \cdot 2H_2O$$

As a result of the hydration and crystallization, the plaster sets and hardens. About 205°C. (400°F.) is a critical temperature in the calcining process. If heated much above this temperature, practically all of the combined water is driven off and the product is known as "hard-burned" or "dead-burned" plaster. Although the plaster is called "dead-burned" and even sometimes "anhydrous," it is generally understood that it is not absolutely so; slight traces of hydrated crystals still remain, which serve as nuclei about which other crystals of hydrated sulfate may form. All plasters that result from calcination at these elevated temperatures are very slow in hydrating; the rate is dependent upon the intensity and prolongation of the heating during manufacture and upon the degree of fineness of the gypsum. For practical purposes, however,

the gypsum is calcined under such conditions that the setting and hardening are not stopped but only greatly prolonged; hydration then requires hours or days, instead of minutes as with plaster of Paris. When finally formed, the hydrated product resulting from these slowly setting plasters is both harder and stronger than that produced by the ordinary plaster of Paris.

Control of Rate of Set.—Because plasters that consist chiefly of the hemihydrate set so quickly that there is not sufficient time for mixing and placing, a retarder must be added to delay the set. Materials employed for this purpose are flour, glue, and similar organic, colloidal substances. The added organic materials act as protective colloids. They form a film about the calcium sulfate particles and impede the hydration, with the result that the crystals do not grow together and cohere so rapidly. Native impurities such as clay, present in the gypsite from which some plasters are made, also act as protective colloids, and therefore as retarding agents.

Classification of Plasters.—On the basis of the degree of dehydration, the gypsum products may be divided into two major classes; these two classes in turn may be subdivided into two subclasses on the basis of whether or not the product is pure or impure. Plasters are frequently classified as follows:[1]

1. Produced by the *incomplete* dehydration of gypsum, the temperature employed not exceeding 205°C.

   a. Produced by calcining a *pure* gypsum; no foreign material is added, either before or after calcining. *Plaster of Paris.*
   b. Produced by calcining a gypsum containing certain natural impurities, or by adding to a calcined, pure gypsum certain materials that serve to retard the setting of the product. *Cement plaster.*

2. Produced by the *complete* dehydration of gypsum, the calcination being carried out at temperatures exceeding 205°C.

   a. Produced by calcining a pure gypsum. *Flooring plaster.*
   b. Produced by calcining at red heat, or above, gypsum to which certain substances (usually alum or borax) have been added. *Hard-finish plaster.*

In commercial classification, the term *calcined plaster* is used to designate a burned plaster to which nothing has been added.

[1] Mills, Hayward, and Rader, "Materials of Construction," 5th ed., p. 264, John Wiley & Sons, Inc., New York (1939).

Calcined plaster may include both plaster of Paris and cement plaster; it is the latter if the original gypsum used was impure.

Plaster of Paris.—As has been indicated in the preceding classification, plaster of Paris is prepared by calcining a pure gypsum to the half-hydrate, without the addition of foreign material. It is usually ground to a fineness such that 80 to 90 per cent will pass a 100-mesh sieve. It sets very rapidly, generally in 5 to 15 min.

Stucco is practically the same as plaster of Paris, since it is made from fairly pure gypsum, but usually it is not so finely ground as plaster of Paris.[1]

Cement plasters are made in a manner similar to plaster of Paris, but they set more slowly because of the presence of retarding agents. The plaster contains a small amount of hair, from 3 to 5 lb. per ton, which has been added to increase its strength and cohesiveness. Some manufacturers employ sisal or manila fiber instead of hair. Cement plaster is used commonly for the base coat, and the hair or other fiber prevents wastage due to excessive dropping of plaster back of the lath.

Since the advent of metal lath, the use of calcined gypsum in wall plasters has met with some objection. Calcium sulfate is a compound that results from the reaction of a strong acid with a relatively weak base; in the presence of water, it dissolves slightly and hydrolyzes to produce an acid reaction. On this account it causes the lath on which it is used to corrode. On the other hand, Portland cement and calcium aluminate, which also set rather rapidly by hydration, have an alkaline reaction and inhibit the corrosion of the metal.

Unless the plaster is made from the earthy variety of gypsum, and therefore already contains clay, it is necessary to add clay or hydrated lime to increase the plasticity and sand-carrying capacity. For this purpose about 15 per cent of hydrated lime is usually added to increase the working qualities of the mass and to stop corrosion.

Since cement plaster, as marketed, contains no sand, two or three parts of sand must be added in preparing it for use. The setting time varies from 1 to 2 hr.

[1] The term "stucco" is used also in a somewhat different sense to indicate a mortar finish on walls. The material used for such work consists essentially of a mortar made of calcined plaster and sand to which a certain amount of lime, fiber, and sometimes coloring matter have been added. Rich mixtures of Portland cement and sand are also included.

Staff.—For temporary buildings, such as are erected for exhibitions, a gypsum plaster called "staff" is employed. It has the same general character as plaster of Paris, but contains fiber of some sort to reinforce and toughen it when set.

Wood-fiber Plaster.—Like cement plaster, wood-fiber plaster also contains an agent to retard the set, but instead of hair about 50 lb. of wood fiber per ton of plaster is employed as a binder. It is designed to be used generally without sand, and finds application where lightness of weight and heat or sound insulation are important. The wood fiber used in the plaster is obtained from non-staining woods such as cottonwood or basswood.

Gypsum Plasterboard.—Plasterboard is a composite material made up of alternate layers of fibrous material, such as wool felt or tough paper, and gypsum plaster. The number of plies varies according to the type of construction for which it is used. During the setting and hardening of the plaster between the sheets of paper or felt, the crystals of the dihydrate that are formed penetrate and interlock through the fibrous layers and bind them together.

Flooring plasters differ from the preceding forms in that they are calcined at such temperatures that they are practically anhydrous. They set very slowly and require very fine grinding, but ultimately they develop great strength and hardness.

Hard-finish Plasters.—Like the flooring plasters, these plasters are practically anhydrous. The velocity of hydration of insoluble anhydrite is greatly increased by the presence of certain salts, such as alum or potassium sulfate. After a preliminary burning at red heat, the calcined product is dipped into a solution of the salt and then reburned. "Keene's Cement" and "Parian Cement" are well-known examples of this type of plaster.

CHAPTER XIII

PORTLAND CEMENT AND CONCRETE[1]

By Thomas R. Alexander, Ph.D.

Portland cement is a finely ground mixture of calcium aluminates and silicates capable of setting and hardening by chemical reaction with water.

Historical.—The Romans made a cement that would harden under water by mixing lime and ground volcanic rock, crushed pottery, or rubble. The first great improvement in cement making is attributed to Smeaton, who undertook the erection of a new lighthouse on Eddystone Rock in 1756. He found that the best mortar for work under water could be made by burning limestone that contained considerable clayey material. In taking the stone from the quarry, however, Smeaton chose those layers that had been shown by test to burn to a lime that would slake with water. Had he ground the unslakable portions he would have produced a cementing material of much more highly developed hydraulic properties.

About 50 years after Smeaton's discovery, Vicat, a French chemist, showed that it was not necessary to depend upon rock in which limestone and clay occurred coincidentally. Vicat produced a hydraulic cement by burning finely ground chalk and clay that had been mixed and made into a paste.

The first patent granted for the making of Portland cement was issued in 1824 to Aspdin, a Yorkshire bricklayer, who heated finely powdered chalk or road dust from limestone roads with the clayey mud of the river Medway. Because the product when set bore a slight resemblance to a well-known limestone from Portland, England, called Portland stone, he named his product Portland cement. Portland cement was first manufactured in the United States in 1875 at Coplay, Pa.

[1] For a comprehensive discussion of Portland cement and concrete, see Lea and Desch, "The Chemistry of Cement and Concrete," Edward Arnold & Co., London (1935).

Materials.—Portland cement is made by fusing together two materials, one calcareous or rich in lime, such as limestone, marl, or chalk, and the other argillaceous, or rich in silica and alumina, such as clay, shale, slate, or blast-furnace slag. Cement rock such as is found in the Lehigh district of Pennsylvania is a clayey limestone that contains both the calcareous and the argillaceous ingredients in nearly the correct proportions.

Manufacture.—Portland cement may be manufactured by either the wet or the dry process. The differences between these methods are mainly in the treatment of the raw materials.

In the dry process, the calcareous and argillaceous materials are coarsely crushed and dried in inclined rotating cylinders, after which they are held in storage bins until analyzed. From these bins, the materials are drawn and mixed in proportions indicated by the analyses, and the mixture is then ground in suitable mills to such a degree of fineness that at least 90 per cent will pass through a 100-mesh sieve. The grinding also produces an intimate mixing of the materials. The mixture is now ready for the kiln in which it is burned.

In the wet process, the materials are crushed and mixed in the presence of water, and ground in the wet condition to a sludge or slurry. After grinding, the slurry, which contains 35 to 40 per cent of water, is stored in tanks. This practice allows corrections to be made in the mixture before burning, with the result that a more uniform product may be obtained. The slurry is fed directly, without drying, into the kiln where it is burned. This saves the cost of the equipment and fuel required for the separate drying operation, but the wet condition of the charge lessens the output of the kiln. With very long kilns (200 ft. or more), the diminution of output becomes less apparent; the charge is dried by the hot gases at the upper end of the kiln.

The wet process is used almost universally in Europe and is rapidly supplanting the dry process in the United States due to the greater accuracy of control of the composition of the mixture.

In both the wet and dry processes the finely ground mixture is heated in a rotary kiln. Kilns are sheet steel cylinders lined with firebrick which vary in length from 60 to 400 ft. or more and are usually from 6 to 12 ft. in diameter. The shorter kilns are used in the dry process. The kiln is inclined at an angle of about 15 deg. to the horizontal, and as it rotates on its axis, the charge, which is introduced at the upper end, travels down. Fuel (powdered

coal, oil, or gas) enters at the lower end, where the hot clinker is partly cooled by the entering air, thus minimizing heat losses. Measurements of kiln temperatures cannot be made accurately, but the maximum is certainly somewhat above 1400°C. (2550°F.). The hot gases that leave the kiln at the upper end come into contact with the entering charge and dry it, thus making separate drying installations unnecessary in the wet process.

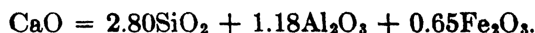
The clinker is hard and glassy and, unless the iron content is very low, it is dark in color. Finely ground clinker (78 per cent must pass through a 200-mesh sieve) sets so rapidly that a retarding agent must be used. The one most commonly used is gypsum, $CaSO_4 \cdot 2H_2O$, which is added to the extent of about 3 per cent and ground with the clinker, thus producing an intimate mixture.

Composition.—As previously indicated, cement manufacturers have a rather wide choice of raw materials. Lime, silica, and alumina are the important ingredients, and any materials that will supply these compounds can be used in cement manufacture provided that they do not contain excessive amounts of other oxides. Iron oxide is present in most clays along with alumina and silica, hence it is present in cement. Magnesium carbonate is associated with limestone, so cements contain magnesia. The following table indicates the range of composition of good Portland cements.

TABLE 78.—COMPOSITION OF PORTLAND CEMENTS

	Per Cent
CaO	60–70
SiO_2	20–24
Al_2O_3	3– 8
MgO	1– 4
Fe_2O_3	2– 4
SO_3	3–11

Practical experience and increased familiarity with the chemical compounds present in cement clinker have made it possible to relate the properties that can be expected of a concrete to the proportions of the various oxides that are present in the raw materials used. The maximum weight per cent of lime, for example, should be related to the percentages by weight of silica, alumina, and ferric oxide in approximately the following way:



$$CaO = 2.80SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3.$$

The ratio of silica to alumina and iron oxides, *i.e.*,

$$\frac{\text{Weight } \% \text{ SiO}_2}{\text{Weight } \% \text{ Al}_2\text{O}_3 + \text{weight } \% \text{ Fe}_2\text{O}_3}$$

should be between 1.7 and 4, depending on the type of cement to be manufactured. The alumina-iron oxide ratio Al_2O_3/Fe_2O_3 varies from 1 to 4 or even higher, again depending on the type of cement. These ratios are called "moduli."

The Burning Process and Compound Formation.—The oxides discussed in the preceding paragraph do not exist in the clinker in the uncombined state. Lime is a basic oxide, silica an acid anhydride; alumina is amphoteric. At the highest temperature of the kiln, compounds are formed which can be identified in the cooled clinker, and the properties of the cement depend on these compounds and on the glassy material that is formed at the same time. The steps in the burning of a charge composed of calcium carbonate, a little magnesium carbonate, clay, or shale, and water are about as follows:[1] (1) evaporation of free water, (2) removal of combined water from the clay, (3) decomposition of magnesium carbonate, (4) decomposition of calcium carbonate, and (5) new compound formation involving lime and clay. Step (1) is complete at low temperatures, but the removal of combined water (2) is quite slow below 500°C. (930°F.). Magnesium and calcium carbonates dissociate when heated into a metallic oxide and carbon dioxide (Chap. XII).



$$MeCO_3 \rightleftharpoons MeO + CO_2$$

The equilibrium pressure of carbon dioxide reaches 1 atm. at about 400°C. (750°F.) in the case of magnesium carbonate and at about 900°C. (1650°F.) when calcium carbonate is heated. These reactions are all endothermic and take place in the upper section of the kiln. As the mixture moves downward into the region of higher temperature, the substances produced in the earlier stages of the burning process begin to react with each other in a highly complicated manner which is not thoroughly understood. Lea and Desch[2] summarize the process of compound formation as follows:

[1] LEA and DESCH, *op. cit.*, p. 102.
[2] LEA and DESCH, *op. cit.*, p. 104.

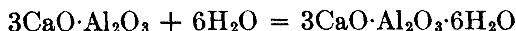
Below 800°C.	Formation of $CaO \cdot Al_2O_3$ and probably $CaO \cdot Fe_2O_3$
800–950°C.	Formation of $5CaO \cdot SiO_2$ and $CaO \cdot SiO_2$
950–1200°C.	Formation of $2CaO \cdot SiO_2$
1200–1300°C.	Formation of $3CaO \cdot Al_2O_3$ and probably $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
1260°C.	Liquid formation starts.
1260–1450°C.	Formation of $3CaO \cdot SiO_2$ with disappearance of free CaO

The chemical compounds that have been identified in Portland cement clinker, together with the names by which some of them were formerly known, and the abbreviations by which they are usually designated are as follows:

Formula	Abbreviation	Name
$3CaO \cdot SiO_2$	C_3S	Alite
$\alpha 2CaO \cdot SiO_2$	C_2S	Belite
$\beta 2CaO \cdot SiO_2$	C_2S	Felite
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	Celite
$3CaO \cdot Al_2O_3$	C_3A	
$5CaO \cdot 3Al_2O_3$	C_5A_3	

In addition to these compounds, the clinker contains an indeterminate amount of glassy material and small amounts of free lime, magnesia, titanium dioxide, manganic oxide, potash, and soda.

The Setting and Hardening of Portland Cement.[1]—Reactions between water and the compounds present in Portland cement lead to the setting and hardening of the material. No exact description of the process is possible, although much information has been gathered regarding the action of water on individual cement compounds. The effects of water are of two kinds: hydration and hydrolysis. The hydration reaction is the one involved when an anhydrous salt such as copper sulfate reacts with water to form the familiar pentahydrate $CuSO_4 \cdot 5H_2O$. Hydrolysis is the term used to describe the reaction between water and a salt which gives an acid and a base. Tricalcium aluminate reacts very rapidly with water giving a hydrated compound.



$$3CaO \cdot Al_2O_3 + 6H_2O = 3CaO \cdot Al_2O_3 \cdot 6H_2O$$

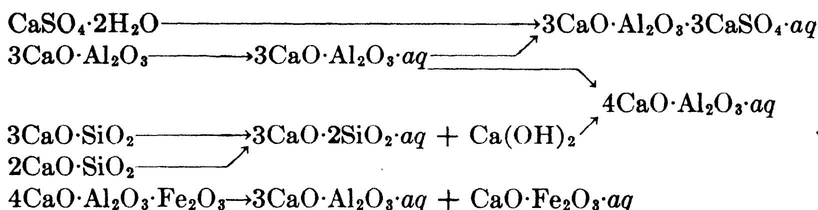
For a detailed discussion see Bogue, "Digest of Literature on the Nature of the Setting and Hardening Process in Portland Cement," Portland Cement Assoc. Fellowship at the National Bureau of Standards, Washington, D.C. (1928).

This reaction is probably responsible for the preliminary set of the cement. Tricalcium silicate reacts more slowly and undergoes both hydration and hydrolysis. No exact equation can be written for the reaction, since there is considerable doubt about the identity of the silicate produced, but the following equation will illustrate the type of change involved:



$$2(3CaO{\cdot}SiO_2) + nH_2O = 3CaO{\cdot}2SiO_2{\cdot}mH_2O + 3Ca(OH)_2$$

This reaction may be responsible for the hardening that takes place during the first few days. Lea and Desch[1] present the following schematic summary of the reactions between water and Portland cement.

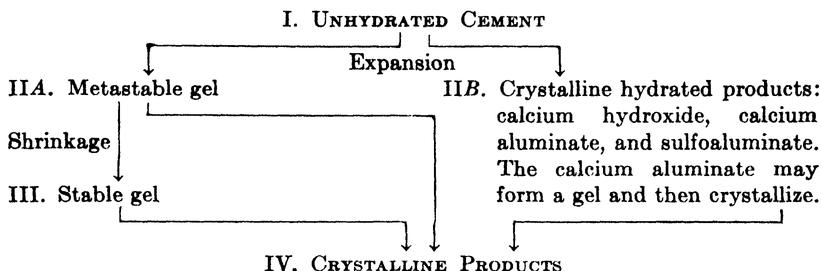


These and other reactions take place during the setting and hardening processes, but a knowledge of the chemical changes involved does not explain the physical changes that the material undergoes.

Two theories have been advanced to account for the solidification of Portland cement. The older one assumes that solidification is due to the formation of a tangled mass of crystals, just as in the case of many other cements. Some colloid chemists, on the other hand, believe that water reacts with the surface of the cement grain to produce a gelatinous material, or gel. The gel serves as a cementing material between the grains, but it loses water slowly to the unhydrated layer underneath and is hardened during the process. This is a very common property of gels, and there is every reason to believe that it plays an important part in the setting and hardening of Portland cement.

It seems certain that the hardening process involves both gel formation and crystallization. Lea and Desch[2] present the following diagram of the process:

[1] Lea and Desch, *op. cit.*, p. 160.
[2] Lea and Desch, *op. cit.*, p. 173.



Initial Set and Hardening.—The following summary of the hydration of Portland cement compounds is given by Klein and Phillips.[1] A short time after the cement is mixed with water, or "gauged," hydrated tricalcium aluminate is produced in amorphous form and later crystallizes. At the same time sulfoaluminate crystals, $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}xH_2O$, are formed; these are produced by the reaction of the aluminate with the gypsum added to retard the setting. At this time the low-burned and finely ground lime also is hydrated.

The next compound to react is the tricalcium silicate. Its hydration may begin within 24 hr. and is generally completed within 7 days. Between 7 and 28 days the amorphous aluminate begins to crystallize and the beta orthosilicate (dicalcium silicate) begins to hydrate. Although the latter is the chief constituent of American Portland cements, it is the least reactive compound. The early strength (24 hr.) of cements is probably due to the hydration of free lime and the aluminates. The increase of strength between 24 hr. and 7 days depends upon the hydration of the tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of the beta-calcium orthosilicate (dicalcium silicate), but here are encountered opposing forces in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that the falling off in strength between 7 and 28 days of very high-burned, high-limed cements is due, whereas the decrease shown by the high-alumina cements is due to the crystallization of the aluminate.

Retardation of Set by Gypsum.—The exact manner in which gypsum retards the initial set of cement is not known. For reasons

[1] "Hydration of Portland Cement," *Nat. Bur. Standards Technical Paper* 43, p. 63.

that are pointed out by Klein and Phillips,[1] the usual explanation that the retardation is due to the formation of the sulfoaluminate crystals that have a selective action on water is insufficient. From their observations it appears that the retarding effect of the gypsum is due to its action as an electrolyte on a colloid solution, *i.e.*, in this case, it prevents the hydrated aluminate from precipitating from its solution to form a gel. They found that with 2 per cent of plaster of Paris, the hydrated substance could coagulate and separate as a solid least readily, with other concentrations of plaster, the separation of the solid occurs in a shorter time, and the set takes place more readily.

Regauging Cement.—Remixing of a set cement destroys the continuous film of gelatinous material produced by the hydration of C_3A. This exposes the unhydrated core to the action of water, and the setting process is repeated. There is little advantage to be gained from regauging a slow setting cement, but a quick setting cement (*i.e.*, one that is high in C_3A) is improved by remixing or by continuous mixing. The effect is the same as that produced by the additions of gypsum.

√**Effect of Fineness on Setting and Hardening.**—Generally the American specifications for Portland cements require that the degree of fineness be such that 78 per cent will pass a 200-mesh sieve. It is very important that the cement be fine. In a cement of normal fineness, only about half the particles are hydrated when the cement has hardened. The reaction with water is always very incomplete because of the impervious coating formed about the grains; the larger the grains, of course, the greater will be the amount of the material unhydrated in the center. If a cement which has once hardened is reground to the specified fineness and then regauged with water, it will develop a very considerable degree of strength due to the hydration of the previously unchanged material. The unhydrated centers of the grains have no function that could not be fulfilled more cheaply by sand. Thus it is evident that the finer cements allow the use of more sand in the mixture.

Other Factors.—A thin mixture of cement and water sets more slowly than one that contains less water because the particles are separated by the excess water. The speed of a chemical change increases with increase in temperature, and the setting and hardening processes in Portland cement are no exceptions to the rule.

[1] Klein and Phillips, *op. cit.*, pp. 29 and 61.

Freezing.—Aside from the disruption of the amorphous binder by ice crystal formation in a wet cement, the hydration process is stopped, and the total amount of water available after thawing will be lessened by evaporation from the ice crystals.

High Early-strength Cement.—Rapid-hardening or high early-strength Portland cement is a cement with a lime content of nearly the theroretical maximum. Fine grinding of the raw materials, grinding and reburning the clinker after adding more lime, and fine grinding of the finished product give a cement that hydrates with greater rapidity. The reactions involved are those of ordinary Portland cement. Portland cements prepared in this way acquire a final set in from 2 to 6 hr.; at the end of 24 hr. the compression strength is approximately 2½ times as great as that of ordinary cement.

High-alumina Cement.—This type of cement is designed to resist the disruptive influences of dissolved salts, especially sulfates, which crystallize from solution in the pores of ordinary Portland cement and cause it to disintegrate. Maximum strength is developed in about 24 hr. The raw materials used in its manufacture are limestone and bauxite (essentially $Al_2O_3{\cdot}2H_2O$). They are completely fused and the resulting slag is drawn off, cooled, crushed, and ground.

The high-alumina cements contain lime and alumina in approximately equal amounts, iron oxide about 15 per cent, and silica not over 6 per cent. The compounds present in the clinker include $CaO{\cdot}Al_2O_3(CA)$, and $3CaO{\cdot}5Al_2O_3(C_3A_5)$, both of which harden rapidly, some $2CaO{\cdot}Al_2O_3{\cdot}SiO_2(C_2AS)$, and a glassy material. $5CaO{\cdot}3Al_2O_3$ has also been identified in the clinker.

The high-alumina cements set much more slowly than the unretarded Portland cements (note the absence of C_3A). The hardening process seems to proceed in much the same manner as in Portland cement, but much more rapidly. Water attacks the calcium aluminates producing gelatinous and crystalline materials. The crystalline material probably contains a large proportion of a hydrated C_2A. Gelatinous material begins to form at once and increases rapidly in amount, acting as a cement between the grains. Crystal formation is somewhat slower. Maximum strength is developed in about 24 hr.

Comparison of Cements.—The following comparison of normal Portland cement, high early-strength cement, and high-alumina

cement is chosen from comparisons of several cements of each type described by Lea and Desch.[1]

TABLE 79.—SETTING TIMES AND TENSILE STRENGTHS OF CEMENTS

Cement	Setting time				Tensile strength,* days			
	Initial		Final					
	Hr.	Min.	Hr.	Min.	1	3	7	28
Normal Portland	1	45	2	35	291	417	542	568
High early-strength	1	00	1	20	480	550	543	619
High alumina	4	30	5	20	532	574	493	514

* Psi. 1:3 mortar.

Testing.—Cements are tested chiefly by mechanical means, the tests usually applied being the test for soundness (constancy of volume), the compression test, fineness, time of setting, and specific gravity. The first two of these are the most important.

The test for soundness is applied to determine whether or not the cement will cause mortars or concretes made of it to disintegrate in any way. The lack of soundness may be due to free or slakable lime, or to coarse grinding. Free lime, in slaking, expands and may cause crumbling. If the quantity present is not too great, it may be rendered inert by air slaking, which may be accomplished by storing the cement for 2 or 3 wk. Thoroughly slaked lime, such as is sometimes added to Portland cement mixtures for waterproofing or for the purpose of increasing its plasticity or smoothness under the trowel, does not have this undesirable effect on soundness. Coarseness of grinding tends to lessen soundness because the hydration of the larger particles is deferred; when it does occur, a disintegrating action may result.

The degree of fineness is determined by sieving. As has been said before, fineness is essential, because only the finer particles are actively hydraulic; the coarser ones merely fulfill the function of sand. The finer the cement, therefore, the greater is the proportion of sand that can be mixed with it.

The determination of the setting rate is important, since in some cements, the initial set may occur before sufficient time has elapsed to allow the mortar or concrete to be placed. On the

[1] LEA and DESCH, *op. cit.*, p. 308.

other hand, after it has been placed, hardening must not be too long deferred, since the longer the time required for the development of hardness and strength, the greater is the chance that it may be injured by accidents.

Storing.—In order that cement may be kept in a condition fit for use, it must be properly stored. It should be kept in an atmosphere as dry as possible and on a raised floor. Moreover, it should be kept covered with canvas or roofing paper. It absorbs moisture from the air quite readily; hence, it should be shielded from moisture-laden currents of air as much as possible. When it has become wet it sets and cannot be used. Lumps are sometimes formed by pressure during storing; such lumps should not be mistaken for lumps caused by dampness. Lumps caused by pressure are readily pulverized.

Concrete

Concrete is composed of coarse material, usually stone, fine material such as sand, in amount sufficient to fill the voids between the lumps of coarse material, and cement and water sufficient to bond the mass. The sand and set cement constitute a mortar which binds the coarser materials together. In order to eliminate voids as completely as possible, the stones and sand must be made up of lumps and grains of varying sizes, so that there will be enough small particles to fill the spaces between the larger ones. The proportions of the different ingredients used vary with the use to which the concrete is to be put. Proportions of cement, sand, and gravel or crushed stone range from 1:2:4 to 1:3½:7 or more.

The properties of the binding mortar are of major importance in concrete, since the rock or coarse material is quite resistant to change. If too much water is used, bonding will be imperfect. The semifluid mortar will flow away from the coarse particles, leaving voids which will increase as the excess water is removed by evaporation. Sand, if too fine, will require an unduly large amount of cement to cover the larger surface. It should be relatively free from organic matter and clayey material.

The stone and gravel used in concrete are usually traprock, granite, and some varieties of sandstone and limestone. Shale, slate, and soft sandstones and limestones do not have sufficient strength to be serviceable. Blast-furnace slag, if used, should be free from iron pellets, since they will corrode if exposed and spoil the appearance of the structure. Since the iron oxide pro-

duced by corrosion occupies a greater volume than the original iron, the expansion may help to rupture the mass. Concrete should not be allowed to dry rapidly, since moisture is essential to the development of high strength. Freezing of the moist concrete must be avoided until it has developed sufficient strength to withstand the disruptive effects of the expansion due to ice crystal formation.

Modern concrete mixing has taken on many of the aspects of an exact science.[1] All materials are carefully chosen for their adaptability to the specific purpose for which the concrete is to be used and processing is exactly regulated and controlled, so that the finished installation will conform exactly to specifications, no matter how large it is. Cement compounds can be varied to suit the particular use to which the cement is to be put. Possible variations are

	Per Cent
C_3S	20–70
C_2S	0–60
C_3A	2–18
C_4AF	0–18

The high early-strength cements referred to previously are examples of the advantage of this type of control. Another example is the manufacture of low-heat cements. Concrete is a poor conductor of heat and, since the setting and hardening reactions evolve heat, large masses may become so hot that they will crack. Since hydration of C_3S and C_3A evolves more heat than the hydration of C_2S, cement with high dicalcium silicate content should be used if heating is to be avoided. Concrete made with cement of this type hardens slowly, so that strains set up by unequal temperatures in the mass are relieved, due to the slow loss of plasticity.

Portland-pozzolan Cement.—Free lime, which is one of the products of Portland cement hydration, contributes nothing to the strength of the cement, as previously noted. If siliceous material of a sufficiently reactive variety, such as volcanic ash, shale, diatomaceous earth, or artificially prepared material be added to the cement, the lime produced during hydration reacts with it to form calcium silicates which are insoluble in water and which do contribute to the strength of the cement. Concretes made with Portland-pozzolan cements are more plastic when freshly mixed, do not segregate so rapidly, and are less permeable than those made

[1] DAVIS, *Mining and Met.*, **20**, 539 (1939).

from ordinary Portland cement. In addition, their heat of hydration is low and they are more resistant to attack by sulfate waters.

Owing to the extensive use of concrete for building structures, bridges, and pavements, the manufacture of Portland cement has become one of the major heavy industries. In 1939, 105,357,000 bbl., 376 lb. each, of Portland cement were produced in the United States.

Waterproofing Concrete[1]

Concrete, as it is ordinarily made, is more or less porous and permeable to moisture. In many of its uses it would be a great deal more efficient if it were not so, as for example, in constructing basement walls and floors, vaults, reservoirs, drains, etc., as well as in all of the reinforced work, the permanency of which would be less doubted if it were waterproof. The corrosion of reinforcing rods would certainly be prevented if moisture were excluded.

A great deal can be done toward making concrete waterproof by merely having the ingredients of the concrete *rightly proportioned*, so that the voids are eliminated. It is said that it can be made entirely waterproof in this manner. In the methods that are commonly employed, however, some special waterproofing material is used. This material is either applied as an external coating, or mixed with concrete before it is placed in the forms.

Dampproofing.—The materials employed in dampproofing are divided into three classes: transparent coatings, opaque cement coatings, and bituminous coatings.

Transparent coatings[2] consist of those materials which do not change the appearance of the surface treated. Perhaps the oldest coating of this class is that produced by alternate applications of solutions of soap and alum or other aluminum salt. As these materials react within the pores, an insoluble aluminum soap is formed, which in addition to being insoluble has a distinct water-repelling property. Because it is necessary to repeat the process a number of times to secure a sufficient amount of the insoluble soap, this method is not economical and is not much used at present. Paraffin wax is another example of the transparent coatings; it may be applied either as melted wax after the exposed surface has been

[1] Bates, *Nat. Bur. Standards Technol. Paper* 3 (1912). Jumper, *J. Am. Concrete Inst.*, **28,** 209 (1932).

[2] For test data, see Kessler, "Exposure Tests on Colorless Waterproofing Materials," *Nat. Bur. Standards Technol. Paper* 248 (1924).

carefully heated, or it may be applied as a solution in petroleum naphtha. Solutions of water glass or sodium silicate are also employed. The silicate is decomposed by the action of carbonic acid, and gelatinous silica is set free in the pores. There is an objectionable feature accompanying this process, in that it is difficult to cause the silicate to penetrate sufficiently. The aluminum, magnesium, and zinc silicofluorides or fluosilicates, known sometimes as *fluates*, are also used.

Opaque Coatings.—Paints are included under this head, but ordinarily paints cannot be safely applied to cement surfaces, since the calcium hydroxide that is set free during the setting of the cement reacts with the oil and destroys the durability of the film. To prevent this destructive action on the oil, the cement surface is first treated with a solution of zinc sulfate which reacts with the calcium hydroxide to produce calcium sulfate and zinc hydroxide. Both of these compounds are quite stable and do not react with the oil. Sometimes a casein paint is used as a first coat before the application of the oil paint, or the casein paint may be applied alone followed by a treatment with formaldehyde to render it waterproof and resistant to molds.

If there is no objection to color, tar makes a very serviceable coating. The tar is heated to expel moisture, treated with lime to neutralize its acidity, and then applied hot, or it may be applied as a paint after thinning it with petroleum naphtha or benzol. Some special bitumens are not used as surface coatings; they are incorporated into the wall. The bitumen is applied before the finishing coat; then a coating of plaster, with which the bitumen forms a very good bond, is applied directly to the bituminous surface.

Waterproofing.—The methods of waterproofing are divided into two classes: the "integral" or rigid method, in which a waterproofing material is incorporated with the concrete mass; and the "membrane" or bituminous-shield method, in which the concrete is insulated from contact with water by the use of a continuous, waterproof, bituminous layer.

The Integral Method.—The materials employed here include hydrated lime and calcium soaps. Hydrated lime may be used for waterproofing with fair success. It has been found that amounts not exceeding 15 per cent may be employed without decreasing the strength of the cement. Moreover, the plasticity and easy-working qualities of the cement are increased. If soap is employed, it may

be previously prepared and added in the dry state, in which case it is very difficult to mix uniformly, or it may be formed in the concrete by using a water solution of sodium soap in place of water alone in mixing.

According to Page,[1] concrete may be made thoroughly waterproof by mixing with it a quantity of heavy mineral oil, equal to from 5 to 10 per cent of the weight of the cement used. This statement has been disputed.

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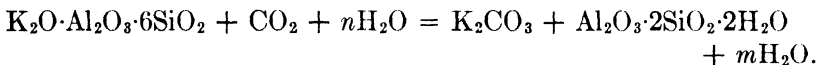
[1] PAGE, *Public Roads, Bull.* 46.

CHAPTER XIV

CLAY AND CLAY PRODUCTS

By Thomas R. Alexander, Ph.D.

Industrially the term "clay" is applied to a mixture of substances, which has resulted from the weathering of igneous rocks, shales, and clayey limestones. The disintegration of clay-forming rock is due to a number of causes. The composition of clay is quite variable, depending on the nature of the rock and on the previous history of the deposit. Clays which have been deposited from water suspension differ from those which remain in the place where they originated. The former usually contain a larger proportion of sand and silt. The formation of clay is largely due to the reaction of water and carbon dioxide on the feldspars, which are found in greater or less amount in most rocks. The term feldspar is applied to a group of minerals which are salts of more or less complex silicic acids, and include the minerals *orthoclase*, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, *albite*, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, and many others such as soda potash and soda-lime feldspars. The reaction between the feldspars, water, and carbon dioxide produces a white mineral called *kaolin* of approximately the composition represented by the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The reaction may be represented by the equation



$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + CO_2 + nH_2O = K_2CO_3 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + mH_2O.$$

The letters n and m in the foregoing equation denote indeterminate numbers of water molecules. The useful properties of clay are due to the fact that kaolin acts as a binder, cementing the particles of sand together.

Plasticity of Clay.—This property makes it possible to mold clay without detaching the particles from one another.[1] As water is added to clay, the plasticity increases until a point is reached at which the particles adhere to other surfaces more firmly than they

[1] For a more complete discussion of plasticity of clay, with literature references, see Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, p. 485, Longmans, Green and Company, New York (1925).

do to each other and the clay becomes sticky. The amount of water required to produce maximum plasticity varies with different clays from as little as 10 per cent to as much as 50 per cent. Addition of more water produces a "slip" or a suspension of clay which can be poured like a liquid. The plasticity of a clay is greatly influenced by the addition of other substances, such as alkalies, salts, and organic acids. Alkalies, organic acids, and some salts increase the plasticity of clay and other salts have just the opposite effect. The plasticity of clay is increased by storage of the damp material.

Drying of Moist Clay.—A molded clay mass must retain its shape on drying in spite of contraction. In the drying process, which must always be slow and uniform, the solid particles become more firmly attached and the object attains considerable strength. This seems to be due to the cementing together of the finely divided materials by moist kaolin. A clay with too great a proportion of kaolin has low tensile strength and must be mixed with sand, previously burned clay, or some similar material to make it serviceable. Air-dried clay will again become plastic when wetted. Shrinkage during drying produces a more compact object and is desirable if the shrinkage is not great enough to produce cracks. Highly plastic clays often show excessive shrinkage on drying and firing. This can be controlled by mixing the clay with sand or previously burned clay.

Burning.—The drying process already referred to removes most of the uncombined water and subsequent "burning" or heating to much higher temperatures, eliminates the chemically combined water, and causes the oxides present to react with each other to form easily fusible glasses, which bond the material and increase its strength. The glassy material is produced by the reaction of "fluxing" ingredients of the clay with silica. The fluxing substances are iron oxide, lime, magnesia, sodium and potassium salts; the glass is a low-melting mixture of silicates of these metals. There is some additional shrinkage during burning with consequent increase in density.

Color of Clay Products.—All clays that contain iron compounds, regardless of color, will burn red if heated in an oxidizing flame. This coloring material is ferric oxide, which is produced by the decomposition of ferric silicate, the decomposition of ferrous silicate with oxidation of the iron to the ferric state, or by the oxidation of iron pyrite. If burned in a reducing atmosphere, ferrous silicate will be produced, and the clay will have a purple cast. Clays free

from iron compounds will probably burn white, since other color-producing oxides are not likely to be present. Buff and cream bricks are made by burning clays containing very little iron oxide. Since the coloring effect of the iron oxide may be overcome by large amounts of lime, cream or buff bricks can be made from clay that is either low in iron oxide or high in lime.

Brickmaking Methods.[1]—The suitably prepared clay may be molded into shape by any one of three methods. These methods are designated as the soft-mud, stiff-mud, and dry-press processes.

In the *soft-mud process* the clay is mixed with water to the consistency of a soft paste and pressed into wooden molds. In order that the brick may be delivered from the mold the more easily, the mold is usually sanded each time before being filled. It is not difficult to recognize soft-mud bricks since they will show five sanded surfaces with the sixth comparatively rough; it is made so by scraping off the excess clay from the top of the mold. Unless repressed, soft-mud bricks lack sharp corners and straight edges. The interior is likely to show more pebbly particles also, than bricks made by other processes.

In the *stiff-mud process* the clay is mixed with just sufficient water to make it plastic, but still quite stiff; then it is forced through a rectangular die in the form of a bar, upon a cutting table. This bar is cut into brick lengths by means of wires. Since the wire makes a somewhat tearing cut, the cut surfaces are always recognizable on a stiff-mud brick. Another characteristic of these bricks that makes recognition quite certain depends upon the manner of mixing the clay. The mixing is done by means of a rotary shaft supplied with blades; the clay is forced through the die by means of a tapering screw. The twisting action resulting from this treatment produces usually a laminated structure within the brick. A stiff-mud brick will have four smooth surfaces and two roughly cut surfaces. Upon the cut surfaces the laminations are sometimes visible.

In the *dry-press process* the clay is allowed to dry in the air until its moisture content is reduced to at least 12 or 15 per cent. The clay is then granulated and screened. After this, it is conveyed to the pressing machine where it is pressed in steel molds. The process produces bricks with sharp edges and smooth surfaces. Such bricks are usually employed for front or face bricks. If the dry-press bricks are not well vitrified in burning they are likely to show a

[1] Ries, "Clays; Their Occurrence, Properties and Uses," 3d ed., John Wiley & Sons, Inc., New York (1927).

granular structure, since the grains of clay cannot coalesce nearly so well as they do when the clay is mixed in a plastic state.

Repressing and Burning.—The soft-mud and stiff-mud bricks are sometimes repressed shortly after molding. The repressing straightens the edges and removes the surface roughness. Usually, also, during the repressing some design is stamped upon the surface of the bricks. Repressing makes the bricks denser and stronger and more resistant to weathering. Most of the common bricks are fired at temperatures ranging from 1050 to 1280°C. (1920 to 2340°F.). The higher temperatures produce vitrified brick which is harder, stronger, and less absorbent.

Rejected Brick.—Because of overfiring or perhaps for some other reason, many bricks come from the kiln discolored, roughened, or twisted. Such bricks must be cast aside and are known as "culls." The brickmaker is rarely able to obtain more than 85 per cent of good bricks from the kiln.

Comparison of Bricks Made by Different Processes.—Soft-mud-bricks are generally more homogeneous in structure than the bricks made by other processes, and they are less likely to be affected by frost action if properly burned. Unless repressed, however, they lack smooth surfaces and sharp edges. Stiff-mud bricks also usually possess a good structure, but laminations may be pronounced and separations may occur between them. The dry-pressed bricks present the most finely finished surfaces. On the other hand, because of their granular structure, if they are not well burned, they are likely to be softer, with less cohesion between the particles than bricks made by other processes.

Efflorescence on Bricks.—Efflorescence is a coating—usually white—that appears on stored bricks or on bricks laid in a wall. It usually consists of the soluble sulfates of magnesium, sodium, and potassium. Sometimes it is due to calcium sulfate, less frequently to sulfates of iron and aluminum. These salts may have been present in the clay or water used to make the bricks, or they may have been produced by the oxidation of minerals during burning. Sometimes they are produced by the reactions of weathering, as by the action of atmospheric sulfur dioxide upon certain silicates existing in the brick. Sulfuric acid may also be produced by the atmospheric oxidation of iron pyrite if it has been left in the brick. In rare cases, efflorescence may be due to mortar.

The incrustation is produced by the leaching out of these salts from the bricks by water; the salts are then deposited upon the sur-

face of the bricks as the water evaporates. Aside from being unsightly, efflorescence exerts a disintegrating effect upon the bricks. The salts that produce it are somewhat hygroscopic and, even when not actually wetted by rains, they dissolve by taking up moisture from the atmosphere and the bricks absorb their solutions. Then, when dry weather arrives, they bring about disintegration of the bricks by the expansive force of their crystallization. During damp or wet weather the efflorescence often disappears; it returns, however, with the coming of dry weather.

The remedy for efflorescence lies chiefly with the maker of the bricks. Water that is free from salts should be used for mixing with the clay. Hard burning, which volatilizes the alkalies and increases the density of the bricks so that less water can find entrance for leaching, is of value. Treatment with barium salts is effective, since the soluble sulfates are converted into insoluble barium sulfate.

It is not an uncommon practice to remove efflorescence by the use of washes containing nitric or hydrochloric acids, but this is very objectionable. Although the incrustation is for a time removed, the real evil is only aggravated. By the action of the acid, the salts present are converted into more soluble forms, which means an increase in the quantity dissolved and a consequent increase in the amount of incrustation left by the evaporated water. The only really successful way is to cut off the source of water supply to the wall. If the wall can be thoroughly dried, good results may be secured by removing the efflorescence with a scratch brush or similar device, and then applying a waterproof coating such as those described for waterproofing cement and concrete (Chap. XIII).

Terra-cotta Ware

Terra cotta means baked earth. This name is applied to a variety of forms of burned clay used for structural purposes. The forms are molded usually from low-grade fire clays and are hard-burned but not vitrified. In this discussion, the terra-cotta products will be considered under three heads: (1) decorative terra cotta, (2) building blocks, and (3) fireproofing.

Decorative terra cotta is either molded in plaster casts or is modeled by skilled artisans. After drying, a coating consisting of clay, quartz, feldspar, and other ingredients, ground in water to the consistency of a thin cream, is sprayed upon the surface. This mixture is known as the "slip layer." In addition to this layer

the ware may subsequently be glazed. The slip layer may be colored and the ware decorated to show various designs.

Building blocks are made usually from clays and shales, or a mixture of these with low-grade fire clays. They are generally hard-burned but not vitrified. No surface coating is applied, since they are used strictly for structural purposes and are then covered by other material, such as mortar or plaster. They are made in a variety of forms, *e.g.*, those known as hollow blocks, furring blocks, hollow bricks, book tiles, etc. They are widely used because of their light weight, and their poor conductivity of sound and heat.

Fireproofing is a general name applied to the hollow ware used for flat arches in floors, for partitions, and for furring in fireproof buildings. It serves to protect the metallic members from the intense heat in case of fire, and so prevents warping and other injury. It serves also as a heat insulator at all times.

Terra-cotta lumber is a name given to that sort of fireproofing that has been made soft and porous by the addition of straw, sawdust, etc., to the clay mixture. The straw and sawdust burn out in the kiln leaving the product in such condition that nails or screws may be readily driven into it.

Other Clay Products

Roofing Tile.—The procedure in making roofing tile is very similar to that followed in the manufacture of pressed bricks. The pressed forms are carefully dried and burned. It is said that a softer-burned tile is a poorer conductor of heat and hence provides a cooler roof, but there is much difference of opinion as to whether a porous or vitrified tile is best. Vitrified tiles have a greater frost resistance and are probably more enduring on this account.

Wall tiles are pressed tiles and may be made from either dry or plastic clay. Those made from dry clay are known as "dust-body" or "dry-press" tiles. The clay used in this process is not dust dry, however, because after it has been dried and pulverized it is steamed to render it slightly moist. Most of the wall tiles are "dry pressed." After pressing, the tiles are set in fire-clay boxes to protect them from direct contact with the flame and then are burned. When burned, the face of the tiles is dipped in a glazing preparation, consisting usually of the silicates of lead, potassium, calcium, and aluminum, ground with water to the consistency of a cream. In this way a transparent glaze is formed. If a colored glaze is desired, the coloring matter is introduced in the form of metallic oxides. By

suitable employment of such oxides, almost any color or shade desired may be obtained. After dipping and drying, the tiles are again fired until the glaze is fused, producing in this way a lustrous surface. Matte or dull glazes also are much used, and these glazes, too, may be colored. The dulled appearance is produced by applying a thick coating of the surface material.

Floor tiles are made by the dry-press process; since they are rarely glazed, only one firing is necessary. Floor tiles may be divided into two kinds—plain and encaustic tiles.

The *plain tiles* are made of one clay throughout; they are burned sufficiently hard to be vitrified or semivitrified. Vitrification results from surface fusion of the component grains. Examples of the plain tiles are the *mosaics*.

The *encaustic tiles* have a facing of one kind of clay and a backing of another. The surface may have a design of several colors. It is first put down in the molding box by the aid of a brass cell frame. The various-colored clays are sifted into this frame, and then the frame is lifted out. When this is done, the mold is filled with a clay backing. Encaustic tiles cannot be burned to vitrification, since the colors are largely dependent upon iron compounds in the clay and such clays burn to buff or red when vitrified.

Sewer pipes are formed from plastic clay in a special form of press. Odd-shaped sections, such as traps and sockets, are usually made by hand in plaster molds. After careful drying the ware is fired. When the kiln has reached a temperature of about 1200°C., common salt, NaCl, is thrown into the fires. The salt volatilizes and, as it comes into contact with the earthenware, reacts with the clay and produces a readily fusible sodium-aluminum silicate which covers the surface of the articles as a glaze. This glaze is known as the "salt glaze"; it is the usual form applied to sewer pipe in the United States. The clay of which the pipe is made must be chosen with this object in view, since all clays will not take a salt glaze. A glaze is sometimes secured by coating the article with an easily fusible "slip clay" consisting of a mixture of litharge, PbO, and clay, or finely ground feldspar, and subjecting the coated article to a white heat.

Drainage tiles are made of red-burning clay by the stiff-mud process; the product issues upon the cutting table as a hollow cylinder, which is divided into lengths by wires. After drying, the tiles are fired, but are not vitrified or glazed since in this care porosity is desired.

Sanitary Ware

Sanitary ware may be divided into two main classes: (1) that produced by the application of a glaze to a clay-product body, and (2) that produced by enameling articles made of cast iron and steel. In both cases it is essential that the coating applied have the same coefficient of expansion as the material composing the body. This, of course, is presumably taken care of by the manufacturer, but sometimes within only certain ranges of temperature. Hence, cracking of the enamel may result from contact with boiling water, when atmospheric changes of temperature would have no effect. None of the ordinary glazes or enamels on sanitary ware are able to withstand the action of the strong acids, such as nitric, hydrochloric, and sulfuric, since they were not made with this object in view. The composition of the enamel is too high in basic oxides, especially of the heavy metals, and too low in silica. By suitably adjusting conditions, however, glazes and enamels can be made that are proof against at least the weaker acids, such as those found in foods.

Vitreous Ware.—That class of ware produced by the application of a glaze to a clay-product body is known as vitreous ware. The body of the ware is made of a mixture of pure, white-burning clay, ground flint, and feldspar. Since this mixture has a yellowish tint, a small amount of cobaltic oxide is added. During the firing of the ware, the cobaltic oxide reacts with silica in the mixture, producing blue cobaltic silicate, which changes the yellowish white of the mixture to a bluish white. The finely ground mixture is worked up into a creamlike fluid, called "slip," is strained to remove coarse particles, is filtered to remove water, and the resulting putty is stored in cellars to "age." Aging increases the plasticity of the clay. When removed from storage, the clay is compressed in a pugging mill to remove air bubbles. From the clay thus prepared, the articles are made by various methods, as by the use of a potter's wheel, by pressing in a mold, or by casting. In many instances, the article is made in sections; the various pieces are then stuck together by means of a little slip and soft clay and the joints are smoothed to as perfect a seam as possible. In a siphon-jet toilet, for example, there may be as many as 16 pieces.

A process that is used for making small articles is known as the *dust process*. For this process, the clay is dried and ground to a fine dust, and then is pressed into shape in steel dies. The buttons

used as index plates on faucets are made in this way. The words "hot" and "cold" are stamped on the button after the first firing.

Before the ware made by any process can be fired, it must be thoroughly dried, an operation that in some instances requires several weeks. When dried, it is placed in rough clay boxes or cases, called "saggers," which are sealed with clay wadding. This is done to prevent the flame in the kiln from coming into direct contact with the ware; if this should happen, the ware would be discolored. When fired, the ware is called "biscuit."

Printing.—If it is desired to have the ware show any printing, it is placed upon it while in the biscuit condition. A clay paste containing an ingredient that will burn to the desired color is prepared and spread upon an engraved copper plate. The excess clay is then removed, leaving only that which lies in the lines of the engraving. Tissue paper is now spread upon the copper plate with even pressure; when the plate is withdrawn the clay adheres to the paper. The paper carrying the color-clay design is laid upon the ware and rubbed with a hard brush, which causes the design to be transferred to the ware. Afterward the paper is washed off.

Glazing.—The mixture for the glaze contains a variety of substances, such as feldspar, flint, kaolin, boric acid, and certain metallic oxides, such as those of zinc, tin, and lead; it is so proportioned that its fusing point is lower than that of the body of the ware or biscuit. The mixture is fused to a glass, ground in water to a creamlike consistency, and then the biscuit is dipped into it. After drying, the ware is fired in a kiln that is not so hot as that in which the biscuit was first fired, but it brings the glaze to its fusing point, so that it fills the pores of the ware with the result that the glaze and body become practically a single mass. Sanitary ware, tanks, lavatories, drinking fountains, etc., are made in this manner.

CHAPTER XV

ABRASIVES

By Thomas R. Alexander, Ph.D.

An abrasive is any substance that can be used to grind away the surface of another substance. The operations of cutting, grinding, and polishing have to be performed on materials of such widely differing hardness and toughness that the abrasive used for one purpose may be quite inadequate for another. Abrasives are either natural or artificial substances but, since their effectiveness depends on physical properties and not on origin, this classification is convenient rather than significant.

The effective use of abrasives in industry is partly an engineering problem and, since this discussion is limited to the chemical aspects of the subject, no attempt will be made to include engineering detail. The natural abrasives will be considered under the three headings indicated in Table 80.[1]

Hard Abrasives

Diamond.—Diamond has a hardness of 10 on the Mohs scale.[2] In addition to diamond dust from gem stones, two varieties of diamond, *carbonado* and *bort*, which are unfit for gem use, are used in grinding, polishing, and cutting operations where great hardness is required. They are used as tips for bits in rock drills, on tools for truing abrasive wheels, as teeth in rock-cutting saws, and on tools for turning hard rubber, fiber, brass, bronze, etc., and for glass-

[1] Eardly-Wilmot, "Abrasive Products of Canada, Technology and Application," Part I, Canada Department of Mines, Ottawa (1927).

[2] The Mohs scale of hardness is an arbitrary scale in which certain minerals are used as standards. In the order of increasing hardness they are (1) talc; (2) gypsum; (3) calcite; (4) fluorspar; (5) apatite; (6) feldspar; (7) quartz; (8) topaz; (9) corundum; (10) diamond. Substances are classified on this scale by their ability to scratch or be scratched by the various minerals listed. The intervals on the scale are quite uneven. For a more complete discussion of the subject see Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, p. 453, Longmans, Green and Company, New York (1923).

Table 80.—Natural Abrasives and Their Uses

Hard Abrasives

- Diamond
  - Crystals — Wheel truing, cutting, and boring
  - Dust — Gem polishing, etc.
- Corundum
  - Manufacturing wheels — Some metals
  - Coated papers and cloths — Some metals and hardwood
- Emery
  - Manufacturing wheels — Snagging metals
  - Coated papers and cloths — Metals and hardwood
  - Loose grain
    - Coated on flexible wheels — Semifinishing and polishing metals
    - Glass grinding
- Garnet
  - Coated papers and cloths — Hardwoods, paint, and varnished surfaces
  - Loose grain — Glass grinding, etc.

Siliceous Abrasives

- Quartz and Flint
  - Burrstones — Grinding grain, paints, etc.
  - Pebbles — In cylindrical mill for grinding ores, etc.
  - Small slabs — Hand-operated, fine sharpening stones
  - Crushed: coated paper or cloth — Soft wood
- Sandstone and Sand
  - Natural grindstone — File, knife, saw, etc., grinding
  - Pulpstone — Wood for pulp making
  - Sharpening stones — Hand-operated, coarse sharpening stones
  - Crushed as loose grain — Sand blasting, glass grinding
- Pumice
  - Blocks — Rubbing paint and varnish surfaces
  - Loose grain — Glass grinding, scouring powders, etc.
- Volcanic dust and pumicite
  - Loose grain — Scouring powders, cleansers, etc.
- Diatomite
  - Powder — Metal polish, dental powder, etc.
- Tripoli
  - Powder — Buffing composition, metal polish, etc.
- Siliceous clay, silt, and rottenstone — Scouring powder, varnish rubbing compounds

Soft Abrasives

- Feldspar, rottenstone
  - Powder — Scouring and cleansing powder, bath bricks, etc.
- Dolomite (lime)
  - Calcined unhydrated in form of grease compound — Buffing of metals, mainly nickel
- Metallic oxides, such as iron, chromium, zinc, tin
  - As red and green rouge, crocus, putty powder, etc., either loose or in form of grease compounds
    - Plate glass, stone, etc., polishing
    - Buffing of metals

cutting tools. The value of industrial diamonds imported by the United States in 1939 was $9,764,579.[1]

Corundum.—Corundum is essentially aluminum oxide. Most samples contain 95.5 to 98.0 per cent of Al_2O_3 along with small amounts of silica, ferric oxide, calcium oxide, magnesium oxide, titanium dioxide, and water. The three principal varieties of corundum are (1) the transparent gem stone (*ruby, sapphire, topaz*); (2) the common or opaque (*a*) block *corundum*, (*b*) crystal *corundum*, associated with many rocks and loose in soil, (*c*) sand *corundum;* and (3) emery.

The abrasive corundum is the opaque variety. Its chief uses, which are not extensive in the United States, are in the grain form for glass grinding and in the manufacture of grinding wheels.

Emery.—*Emery* is a mixture of corundum and *magnetite.* It is an opaque, massive mineral, dark gray to black in color; its composition is usually with the following limits:

TABLE 81.—COMPOSITION ON EMERY

	Per Cent
Al_2O_3	50–70
SiO_2	1–7
Fe_3O_4	20–40
CaO	0.5–1.0
MgO	0.0–5.0
H_2O	1.0–5.0

The hardness of emery depends on the proportion of corundum which it contains. The coarseness of grain is also largely determined by the size of the corundum crystals. There are three grades of emery: Grecian, Turkish, and American.

Grecian emery has the highest aluminum oxide content. The grains are hard and sharp, and since it is not damaged by heat, it is used in grinding wheels where temperatures may be somewhat high. Turkish emery contains about 25 per cent of iron oxide. It is slightly softer and more brittle than the Grecian emery. Its grains break under pressure, producing fresh, sharp edges. It is used in glass grinding and beveling, and for polishing. It does not withstand heat well, hence it is not often used in grinding wheels. American emery may contain as much as 45 per cent of iron oxide and is much the softest of the three varieties. It is used chiefly for wood or soft metal work. Seven hundred and sixty-five short

[1] METCALF, "Minerals Yearbook," 1940, p. 1283, U.S. Department of the Interior, Washington, D. C.

tons of emery were sold or used by producers in the United States in 1939.

Garnet.—The common abrasive garnet is *almandite*, $Fe_3Al_2(SiO_4)_3$, and *grossularite*, $Ca_3Al_2(SiO_4)_3$. Garnet is used in the intermediate "fining" step between sanding and rough polishing of plate glass. Small amounts are bonded into wheels with silicate or shellac binder. Vitrified binder cannot be used because of the low melting point of the garnet. Abrasive garnet sold or used by producers in the United States amounted to 4,056 short tons in 1939. There were no imports.

Siliceous Abrasives

Before discussing the various siliceous abrasives listed under this heading in Table 80 and their uses, it may be well to emphasize the fact that nearly all of them are more or less pure silica. This substance is found in nature in many forms and many different states of aggregation, ranging from crystalline deposits of quartz and massive deposits of noncrystalline varieties to very finely divided material which consists of the siliceous skeletons of aquatic plants. Sand, as used in this discussion, will refer to siliceous sands. The word itself refers to the state of division of any material and not to its composition.

Quartz, Flint, Chert, and Quartzite.—These are all forms of more or less pure silica. *Quartz* is a crystalline substance which is quite brittle and has a hardness of about 7. *Flint* and *chert*, which are not sharply differentiated, are not crystalline. Flint is nearly as hard as quartz. *Quartzite* is a metamorphosed sandstone which is nearly pure silica. It is harder and more dense than sandstone and the grains are not easily distinguishable. Burrstone is a cellular, hard, tough variety of quartzite. It was formed by the dissolving away of calcareous cementing material which was probably of fossil origin. Stones made from this material were formerly used for grinding grain, but are now used mostly for grinding paint pigments. Their use is declining due to replacement by artificial grinding agents.

Pebbles.—Like the word sand, this word describes the size of the material rather than its chemical composition. The grinding operation referred to in the chart employs a horizontal rotating cylinder which may be lined with solid blocks of quartz, quartzite, or chert. Rounded flint pebbles or steel balls are put into the cylinder along with the material to be ground. The cylinder is

then rotated until grinding is complete. The use of pebbles and silica liners in grinders is of particular advantage in the grinding of ceramic materials which must not be contaminated by iron. The United States production of pebbles and liners is not sufficient to meet the demand.

Small Sharpening Stones.—Small sharpening stones for hand operation include oilstones, whetstones, scythestones, hones, and rubbing stones. The selection of the stone depends on the type of tool to be sharpened and the edge desired. Many stones, particularly those sold for domestic use, are made from a mixture of natural grits bonded by clay, water, and sodium silicate. After mixing, the material is pressed into molds and baked.

Oilstones.—Natural oilstones are made from very fine grained sandstone. One of the best minerals for this purpose is novaculite, a sedimentary rock containing about 99 per cent of silica. It consists of minute, interpenetrating, sharp-edged crystals with small spaces between, which gives it a superior cutting power. The finer grained stones are used by physicians, dentists, and others for sharpening very fine edged instruments. Other natural sharpening stones are made from sandstones (see Chap. XI) of various grain sizes, depending on the use to be made of them.

Sandstone and Sand.—Stone for use in grindstone and pulpstone manufacture should be taken from beds that are thick and free from cross joints. The stone should be of uniform hardness throughout; the grains should be even and sharp; and it should be free from clay or other substances that reduce its strength. A soft stone wears away quickly and does not grind evenly; a very hard one cuts slowly because the edges of the grains become rounded. The silica grains should be cemented together firmly enough to give the necessary strength to the stone, but should be dislodged easily enough to expose fresh, sharp grains continuously. The size of the grit determines the nature of the cut. Cementing materials are usually limonite, clay, calcite, and quartz.

Pulpstones.—These stones are used to grind or shred wood for papermaking. They are grindstones with large faces, ranging in size from 26 to 54 in. thick and from 54 to 62 in. in diameter. The stone must cut, or rather tear, the barked wood rapidly and have a long life. It must also wear evenly to avoid strain on the rotating machinery, since the stones weigh from 2 to 4 tons and rotate rapidly. Pulpstones must be aged or cured before use to remove the quarry water and improve cementation. Chaser stones

are large circular stones which run on edge over the material to be crushed, which is spread out in a container of some hard material. This type of stone is used extensively in mineral grinding. Some chaser stones are made of granite and others of sandstone. Some United States production and price data for 1939 are given in Table 82.

TABLE 82.—PRODUCTION OF STONE ABRASIVES*

	Short tons	Value
Grindstones	7,917	$257,350
Pulpstones	2,517	169,025
Oilstones, whetstones, etc.	620	115,805

* METCALF, *op. cit.*, p. 1278.

Sand.—Grinding and polishing sands are tough, sharp, hard sands, free from clay. They are used for cutting and polishing stone, grinding glass, sandpaper manufacture, and sandblasting.

Pumice.—Pumice is a glassy volcanic lava with a cellular structure caused by steam and other volcanic gases. It occurs in solid blocks of low specific gravity (the dried blocks will float on water) and of varying porosity and coherence.

Pumicite.—Pumicite is a volcanic dust of about the same composition as pumice, which can be used for the same purposes as ground pumice. The grains are sharp and angular, and vary in size. It is often mixed with sand, clay, silt, etc., and is sometimes cemented with calcium carbonate. Beds vary in thickness from a few inches to 100 ft.

TABLE 83.—COMPOSITION OF PUMICE AND PUMICITE*

	Per Cent
SiO_2	67–80
Al_2O_3	12–17.5
Fe_2O_3	0.5–2.5
FeO	0.2–4
MgO	0.0–2.3
CaO	0.5–3.0
Na_2O	1.5–3.0
K_2O	1–5
H_2O	1–8

* EARDLY-WILMOT, "Abrasives," Part I, p. 80, Canada Department of Mines, Ottawa (1927).

Pumice in lump form is used as an abrasive for rubbing down wood and metal surfaces and paint and varnish finishes. Ground

pumice and pumicite are used in many domestic and other cleaning, scouring, and polishing preparations such as hand soaps, silver and other metal polishes, and tooth pastes and powders. Pumice and pumicite used in cleaning and scouring compounds and hand soaps in 1939 in the United States amounted to 52,500 short tons valued at $227,447. Other abrasive uses consumed 5,500 short tons.

Diatomite.—Diatomite (also known as diatomaceous earth, infusorial earth, kieselguhr, etc.) is composed of the siliceous remains of minute aquatic organisms called diatoms. It is a light, finely granular, porous aggregate which varies from a loosely coherent to a compact form. It has the general appearance of chalk and the purer deposits contain up to 96 per cent of silica. As an abraisve it is used in paste and liquid metal polishes, dental powders, etc.

Tripoli and Amorphous Silica.—Although tripoli resembles diatomite, it is of an entirely different origin. It is derived from the alteration or decomposition of chert or of highly siliceous sandstone. It is soft, porous, highly absorbent, and easily crushed, with a silica content of 96 to 99 per cent. The name is frequently and incorrectly applied to other forms of silica that resemble tripoli. In addition to its use in cleaning and scouring preparations, tripoli is a frequently used abrasive in so-called "grease bricks" or "compounds" which contain the abrasive bonded with stearic acid, paraffin, or tallow.

Soft Abrasives

Abrasives in this group are nonsiliceous. Although they are softer than the materials to be abraded, they smooth and polish metal and other surfaces very effectively. Buffing, which is the final stage of polishing, is done with a rapidly revolving, flexible wheel made of cloth or leather and coated with the abrasive.

Rottenstone.—This material resembles tripoli in many of its properties. It is a residual product of the weathering of siliceous-argillaceous limestone, hence its principal ingredient is aluminum oxide (80 to 85 per cent), with 4 to 15 per cent of silica and 5 to 10 per cent of iron oxide. Most of the true rottenstone used in the United States is imported, but another rock called Pennsylvania rottenstone is used extensively for the same purposes. It contains about 60 per cent of silica, 17 to 18 per cent of alumina and 9 per cent of iron oxide, with some calcium oxide and alkali metal oxides.

Vienna Lime.—This soft abrasive is produced by the careful calcination of very pure dolomite. It is quite soft and free from grit and is used to give metal surfaces a very bright finish.

Metallic Oxides.—More or less highly hydrated ferric oxide is used for buffing metals and for glass polishing. *Crocus* is a hard reddish-purple oxide with a sharp grain. *Rouge* is softer, with rounded grains, and is used for finer polishing. *Black rouge* is the magnetic oxide of iron, Fe_3O_4. *Green rouge* is the oxide of chromium, Cr_2O_3. It is also used to produce a high finish. "Putty powder" is an oxide of tin, SnO_2. It is not used extensively. *Satin rouge* is lampblack.

Artificial Abrasives

The artificial abrasives of greatest importance are silicon carbide, SiC, sold under the trade names Carborundum and Crystolon; fused aluminum oxide, Al_2O_3, called Alundum and Aloxite; boron carbide, B_4C, and steel shot, crushed steel, and steel wool. Rouge, which has been discussed previously, might also be included in this group.

Silicon Carbide.[1]—Silicon carbide was discovered by E. G. Acheson in 1891. It is made by heating a charge of silica sand and carbon to a high temperature in a resistance furnace. Low-sulfur coke, anthracite coal, or petroleum coke supplies the carbon. The sand, which should contain at least 98 per cent of SiO_2, and the coal or coke are mixed in about the proportions indicated by the equation $SiO_2 + 3C = SiC + 2CO$. Some sawdust is frequently included to increase the porosity of the mass so that the CO may escape more readily.

A typical furnace is 47 ft. long, 8 ft. high, and 8 ft. wide, with curved side walls so that the furnace is roughly cylindrical. The initial voltage is between 200 and 300. The furnace must be taken down to remove the charge which consists of a core of graphite surrounded by a crystalline mass of SiC. The crystalline material merges into a layer of amorphous material composed of uncrystallized SiC and a number of compounds of silicon, carbon, and oxygen, and that is surrounded by an outer layer of unchanged charge which can be recovered and used. After the crude SiC has been crushed, it is treated with boiling H_2SO_4 and then with NaOH

[1] Mantell, "Industrial Electrochemistry," 2d ed., Chap. XXIV, McGraw-Hill Book Company, Inc., New York (1940).

solution. This treatment removes silicon and the silicides of iron and aluminum as well as graphite.

Silicon carbide is between corundum and diamond in hardness. The crystals are very brittle, but as they wear away they continue to present extremely sharp edges, so that their cutting power is not reduced. It is unreactive chemically and able to withstand the action of high temperatures without damage. As an abrasive it is used in grinding wheels for cast iron, brass, stone, and glass, on coated paper and cloth, and for small sharpening stones. Silicon carbide production in the United States and Canada in 1939 was approximately 24,000 short tons, of which about 70 per cent was used for abrasive purposes.

Fused Aluminum Oxide.[1]—Fused Al_2O_3 is similar in most respects to corundum. The raw material used in its production is bauxite, a hydrated Al_2O_3 which is also the source of metallic aluminum. The Al_2O_3 crystals, which form as the molten mass cools, are cemented together by small amounts of other oxides which were either present in the original bauxite or were added for the purpose. If coke and scrap iron are added to the aluminum-bearing material, foreign oxides will be reduced and the resulting free elements alloyed with the iron will sink to the bottom, leaving a slag of fused Al_2O_3 on top. This process is useful when the percentage of oxides other than Al_2O_3 is too high. It removes sulfur, phosphorus, iron, titanium, and silicon. The charge is fused in an arc furnace with a removable outer shell which can be lifted away from the ingot of fused Al_2O_3 when the operation is complete. Preparation for the market involves crushing and treatment with acid and alkali, as well as magnetic separation. Fused Al_2O_3 is used in grinding wheels and in coatings for abrasive paper and cloth. The total production in 1939 in the United States and Canada was about 50,500 short tons of which about 96 per cent was used for abrasive purposes.

Boron Carbide.—This substance was first proposed for commercial use in 1934.[2] Its preparation is similar to that of silicon carbide. Coke and B_2O_3 are heated to 2500 or 2600°C. in a resistance furnace where they react as follows: $2B_2O_3 + 7C = B_4C + 6CO$. It is highly crystalline, unreactive, heat resistant, and harder than silicon carbide.

[1] MANTELL, *op. cit.*

[2] RIDGEWAY, *Trans. Electrochem. Soc.*, **66**, 117 (1934).

Metallic Abrasives.—Steel shot is used in the smaller sizes for blast cleaning of castings, forgings, etc. Coarser shot is used in core drilling and in sawing, grinding, and polishing stone. Steel grit is crushed steel. It is angular in shape and is used in sawing and grinding stone. Finer sizes are sometimes used in grinding optical glass. These abrasives are used instead of sand for blastings. Some of the advantages claimed for them are greater durability, lower handling costs, and decreased dust production.

Grinding Wheels, Coated Paper and Cloth

Both natural and artificial abrasives are used in the manufacture of wheels, coated paper and cloth.

Wheels.—There are five types of bond used in the manufacture of grinding wheels: vitrified, silicate, elastic or shellac, synthetic resin, and rubber. The ceramic or vitrified bond, which is the most important, is produced by mixing ceramic raw materials (clay and feldspar) with water and the abrasive grain. After mixing and molding, the wheel is dried and fired in a kiln until the ceramic materials have formed a glassy bond. The vitrified bond is very strong—in fact it is to some extent an abrasive itself. The wheels are highly resistant to chemical attack and to moderate temperature changes. The silicate bond is made by mixing the abrasive with sodium silicate solution. Evaporation causes coagulation of the silicic acid which separates as a jellylike mass, and hardens to form a bond. After hardening, the wheel is baked. The silicate bond is softer and less heat resistant than the vitrified bond, but the wheels are very satisfactory for many purposes, such as cutlery and edged tool grinding. The shellac bond is made by incorporating the grit with melted shellac and allowing it to solidify. The solid is then broken into lumps which are placed in closed molds and warmed until the shellac has taken the form of the mold. Shellac wheels are always thin and are used only for very fine work. They do not resist strain or high temperatures.

Synthetic resins are in many cases superior to shellac as bonding material; in some cases they have replaced the vitrified bond. The exact method of preparation depends of course on the resin used. These wheels can be operated at very high speeds and are adapted to a great variety of tasks. Rubber-bonded wheels will function only when enough heat has been generated to melt the rubber away from the surface of the grains, hence they are always operated at high speeds.

Coated Papers and Cloths.—These are made by sifting the abrasive onto the paper or cloth which has been covered with a layer of soft glue. After drying, the sheet is again coated with very thin glue.

REFERENCE

TONE: *Chem. Industries*, **15**, 133 (1939)

CHAPTER XVI

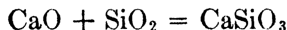
GLASS

By THOMAS R. ALEXANDER, PH.D.

Any substance or mixture of substances that has solidified from the liquid state without crystallization is a glass. Elements, compounds, and mixtures of widely varying composition can exist in the glassy state, but the term "glass" as ordinarily used refers to material which is made by the fusion of mixtures of silica, basic oxides, and a few other compounds that react either with the silica or with the basic oxides. No definite chemical compounds can be identified in glass. Many of its properties correspond to those of a supercooled liquid whose ingredients cannot be identified because they have not separated from the solution in crystalline form.

Types of Reactions.—Although the chemical identity of the compounds present in glass cannot be established, some of the fundamental chemical changes that take place during the melting process can be illustrated by reference to some known reactions between the substances used in glassmaking. These examples must be regarded as illustrations of the types of reactions involved rather than exact descriptions.

The reaction between a basic oxide and an acidic oxide or acid anhydride yields a salt. At high temperature lime reacts with silica to form calcium silicate.



$$CaO + SiO_2 = CaSiO_3$$

The same reactants, if present in different proportions and heated to higher temperatures, may produce salts of different composition.[1]



$$3CaO + 2SiO_2 = Ca_3Si_2O_7(3CaO \cdot 2SiO_2)$$



$$2CaO + SiO_2 = Ca_2SiO_4(2CaO \cdot SiO_2)$$

Another important reaction is the one between silica and sodium carbonate, or soda ash.



$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

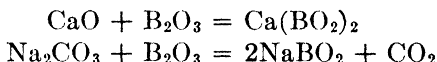
[1] MELLOR, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, p. 348, Longmans, Green and Company, New York (1925).

Other salts, such as Na_4SiO_4, can also result from the reaction between these two substances. Limestone, $CaCO_3$, and dolomite, $CaCO_3 \cdot MgCO_3$, react with silica forming silicates and carbon dioxide. Sodium sulfate or salt cake, Na_2SO_4, also reacts with silica, but only at higher temperatures. Carbonaceous material (usually powdered coal) is added to reduce the sodium sulfate to sodium sulfite, which reacts more readily.



$$Na_2SO_3 + SiO_2 = Na_2SiO_3 + SO_2$$

Sodium nitrate (nitre cake) is used in glassmaking because of its oxidizing action and its low melting point. Lead is introduced into glass as litharge, or lead oxide, PbO. The commercial product usually contains some red lead, Pb_3O_4. Lead silicates, $PbSiO_3$ and Pb_2SiO_4, for example, are formed when lead oxide and silica are heated together. Potassium carbonate, K_2CO_3, is the potassium compound most frequently used in glass manufacture. Its reactions are similar to those of sodium carbonate. Boron oxide, B_2O_3, is an important ingredient of heat- and corrosion-resistant glass. It reacts with the basic oxides to form borates.



$$CaO + B_2O_3 = Ca(BO_2)_2$$
$$Na_2CO_3 + B_2O_3 = 2NaBO_2 + CO_2$$

"Cullet" or waste glass is also added to the batch. Aside from the economy involved, it serves as a flux, since its melting point is lower than that of the ingredients of the batch.

Melting.—When the well-mixed raw materials are heated in the glass furnace, those substances with the lower melting points liquefy and act as solvents for other substances, at the same time reacting with them and enabling them to react with each other. The system is a very complicated one, and the exact sequence of events cannot be determined. The temperature during melting is kept as high as practical (1400 to 1500°C. or 2550 to 2730°F.) in order to reduce the viscosity. Bubbles of gas (carbon dioxide, steam, etc.) that are formed during the heating must escape, and their escape will be slower from a more viscous liquid. In order to remove the gases entirely, the glass must be held for some time at the highest possible temperature. This is called "plaining" or "fining." Additions are often made to the batch to lower its viscosity and to generate gas in large volumes at later stages in the melting process, thus sweeping out the small bubbles along with the large ones. Salt cake is often used for this purpose. The

undecomposed portion forms a liquid layer on the surface of the glass and reacts with the scum of siliceous material that tends to collect there.

The *working temperature, i.e.*, the temperature at which the glass has the proper viscosity for the shaping operations, is much lower than the highest temperature during melting, the actual working temperature being dependent on the kind of glass and the type of machine used. The range is roughly from 1000 to 1300°C. (1830 to 2370°F.), or higher.

Properties of Glass

In spite of the wide variety of uses, ranging from fabrics to building blocks, to which the commercially important glasses are adapted, they have many properties in common and are limited in composition to a small number of ingredients. Sharp[1] gives the following requirements which a commercial glass must meet: (1) The material must melt at commercially obtainable temperatures. Fused silica cools to a glass that is superior to ordinary glass, but the temperature required to melt it is so high that its production is expensive and its use restricted. (2) The molten mixture must remain in the amorphous or noncrystalline condition after cooling. The failure of the fused mixture to separate into definite crystalline compounds on cooling is due in part, at least, to the fact that the viscosity of the melt is very great in the temperature range where such separation is to be anticipated. Crystallization involves the orderly arrangement of ions and molecules in a precise geometric structure. In a viscous medium mobility is less than it is in a more fluid one such as water and the crystallization process is impeded. *Devitrification* is the term used to describe the crystallization of glass. Glass can be made to crystallize or devitrify by keeping it hot for a length of time that varies with the kind of glass. (3) The fluidity of the molten glass must persist to a sufficient extent to permit the formation of desired shapes while the glass is cooling. Since the length of time required for shaping and the most desirable degree of fluidity vary with the method of handling, this property of the glass must be adapted to the manufacturing methods used. The introduction of automatic-machine processes for the shaping and handling of glass has necessitated many changes in the composition of the material used. (4) The glass must be reasonably permanent in the use for which it is

[1] Sharp, *Glass Ind.*, **21**, 158 (1940).

intended. Glass with a high proportion of sodium oxide is more readily attacked by water and acids than glass that contains less sodium oxide and more lime and magnesia. Glasses low in basic oxides are less readily attacked.

Composition of Glass[1]

Soda-lime Glass.—This type of glass is the one that is produced in largest quantity. Its principal uses are for window glass, plate glass, and container glass (bottles, jars, etc.). Its composition, like that of most glass, is not rigidly fixed, but can be varied both as to the amounts of ingredients and the chemical compounds used. The variability of composition is shown in the following tables which give the range of composition of various soda-lime glasses that are satisfactory for use and are adapted to the type of machine employed.

Percentage Composition

	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3
Window glass	73 (approx.)	15–16	......	6–8	2–4	1
Rolled plate glass	71–73	13–17	......	11–14	0–1.5	
A container glass*	74	17.0	......	5.0	3.5	0.5
Light-bulb glass	71.5–73.5	14–17	0.0–1.5	5–6	3.5–4.5	1–2

* Glass of about the same composition is used in the manufacture of the cheaper varieties of tableware.

Flint Glass.—This is a potash-lead glass used for the better quality of tableware and for optical glass. It liquefies at a lower temperature than soda-lime glass and has greater luster. Owing to the ease with which lead compounds are reduced, the glass must be melted in an oxidizing atmosphere. The compositions of two flint glasses are as follows:

Percentage Composition

SiO_2	PbO	CaO	Na_2O	K_2O
73.1	7.1	2.0	12.7	4.6
67.2	14.8	0.9	9.5	7.1

Glass to be used for the more expensive tableware has a lead oxide content of from 15 to 30 per cent and the alkali is K_2O.

[1] Sharp, *Ind. Eng. Chem.*, **25**, 755 (1933).

Borosilicate Glass.—Both soda-lime and flint glass are unable to withstand sudden temperature changes because of their large coefficients of thermal expansion. The basic oxides that they contain make them susceptible to chemical attack by water and acids. Elimination of the basic oxides and inclusion of boron oxide produces a glass that is very resistant to thermal shock and to attack by water and acids. The temperature required to melt and fine such a glass is so high that it has to be heated in the electric arc. The familiar Pyrex glasses, which are used extensively for cooking utensils and laboratory ware, are borosilicate glasses. The following is the analysis of a typical Pyrex glass.

PERCENTAGE COMPOSITION

SiO_2	B_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O
80.5	11.8	2.0	0.29	0.06	4.4	0.10

Vitreous Enamels.[1]—Kitchen utensils, tubs, and many other articles made from stamped sheet steel are coated with a glassy enamel. The glass in finely divided form is dusted on the red-hot metal, where it melts and forms the coating. The glass must be rather high in soda to make it soften at the temperature of the steel, and its composition must be so regulated as to give it a coefficient of thermal expansion approximately that of the metal to avoid cracking (page 461).

GLASS FURNACES

Refractories.—One of the difficult problems in glass manufacture has been to find materials for furnace construction that will resist the action of molten glass, retain the heat that is being supplied, and sustain the necessary weight at high temperatures. All refractory materials that are practical for glass furnaces are attacked by molten glass, since they contain some of the ingredients of the glass itself. Fire clay of the proper composition is the most satisfactory material. The clay must not deform at temperatures as high as 1600°C. (2910°F.). It must have enough fusible material in it to form a glassy bond, which contributes to the strength of the block, and it must become plastic when mixed with water. This latter property makes it possible to cast or mold shapes whose

[1] WHITE, "Engineering Materials," p. 341, McGraw-Hill Book Company, Inc., New York (1939).

consistency is uniform throughout. The addition of burned clay or "grog" promotes uniform drying and prevents shrinkage during firing. Other reinforcing agents are also used, the most important being the mineral *kyanite*, $Al_2O_3 \cdot SiO_2$. Lack of uniformity in the finished block causes pitting and channeling, due to uneven resistance to attack by molten glass, with consequent reduction in the life of the wall. Blocks of cast *mullite*, $3Al_2O_3 \cdot 2SiO_2$, have come into use recently as refractories in the glass industry. They are made by the complete fusion of materials approximating the mullite composition in the electric arc. The solidified product contains crystals of mullite, corundum, Al_2O_3, and a glassy bond. Two types of glassmaking furnaces are in general use: the tank furnace and the pot furnace.

Tank Furnaces.—In the continuous tank a constant level of molten glass is maintained by the addition of raw materials or "batch" at the proper rates. The furnace is divided into two compartments: the larger melting compartment and the smaller working compartment from which the molten glass is withdrawn. Molten glass flows from the melting to the working compartment through a small opening at the bottom of the dividing wall. The "day tank" is a smaller tank, designed to complete the melting of a small charge in one day. It is a particularly useful type of tank in cases where frequent changes in glass composition are required.

Pot Furnaces.—This type of furnace is used to make small amounts of glass such as optical glass, that require careful control of ingredients and of melting and fining operations. The pots are fire-clay crucibles ranging up to 3 ft. in height and up to 5 ft. in diameter. They are arranged on ledges in a circular or oblong furnace where they are exposed to a steadily increasing temperature until the process is completed.

Annealing.—The removal of internal strain produced by too rapid solidification of the surface of the molten material is a problem frequently encountered. In annealing glass, the piece is heated until it is fluid enough to be relieved of strain in a reasonable length of time, and then cooled at a rate that will reintroduce a minimum of strain. Accurate control of both heating and cooling is necessary in the annealing process.

Colored Glass.[1]—Coloring agents in glass are of three types: (1) substances that dissolve in the glass and cause the absorption

[1] PHILLIPS, "Glass, the Miracle Maker," p. 45, Pitman Publishing Corporation, New York (1941).

of certain light frequencies by the glass; (2) precipitated particles of submicroscopic (colloidal) size; and (3) larger particles. The first group includes the oxides of many metals, particularly the transition metals such as nickel, cobalt, iron, manganese, chromium, and some others. The color produced by a given oxide depends on the composition of the glass and the state of oxidation of the metal. If nickel oxide is dissolved in a glass that is high in boron oxide, the color will be yellow; in a potash-lime glass the color is reddish violet. The color produced by cobalt oxide ranges from purple to blue. The lower oxide of chromium, Cr_2O_3, gives the glass a green color, but if the glass is basic, oxidation will convert the Cr_2O_3 to chromate and the color will be yellow. When copper oxide, CuO, is dissolved in glass, the color produced is a greenish blue. In a reducing atmosphere, however, cupric oxide will be reduced to cuprous oxide, Cu_2O. This oxide, when heated, decomposes as follows:



$$Cu_2O = CuO + Cu$$

The resulting color, called copper ruby, is due in part to the copper oxide (type 1) and in part to the colloidal copper (type 2). Ferrous oxide, FeO, gives glass a green color and also makes it strongly heat absorbent. Since ferric oxide, Fe_2O_3, gives glass a yellow color, it is possible to change the green iron color to the less objectionable yellow by oxidation. The green color can also be masked by other colors but this method reduces the amount of light transmitted.

Glasses of a great variety of compositions, colors, and physical forms have found specific industrial uses: glass wool and fabrics woven from glass fibers are used as heat and electrical insulating materials (Chap. XXI); plates of glass laminated with a layer of transparent plastic are shatterproof ("safety glass"); glass blocks and "tempered" glass panels have become important building materials. The limitations of space make it impossible to give an account of even the most important of these special applications, and the reader must be referred to the larger treatises.

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CHAPTER XVII

ORGANIC PLASTICS

By G. H. STEMPEL, JR., PH.D.

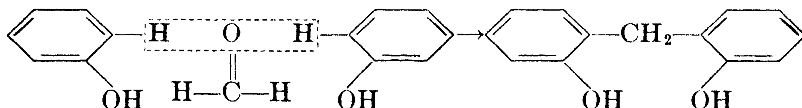
Organic plastics are comparatively new materials of construction for which a rapidly increasing number of industrial applications are being found. Plastics derive their name from their existence, at some stage of their formation or fabrication, as plastic masses capable of being shaped by flow induced by either heat or pressure, or both. Although there are available a wide variety of properties in the various plastics, it may be said that in general they have found greatest utility because of their low specific gravities, ease of fabrication, resistance to solvent action, and low thermal and electrical conductivities. Many plastics have high colorability and afford a wide range of color for decorative use; others are completely transparent and have relatively high refractive indexes that make them suitable for optical purposes.

Plastics may contain a number of constituents including binders, fillers, dyes or pigments, plasticizers, lubricants, solvents, and catalysts. A plastic is usually classified according to the kind of binder used in its manufacture. It is the binder too that determines the type of treatment necessary to mold articles from the plastic. As its name implies, its function is to hold the other constituents together and it may compose anywhere from 30 to 100 per cent of the plastic.

Binders may be either synthetic (or natural) resins or cellulose derivatives. Chemically both kinds of material may be described as substances made up of very large molecules. These supermolecules are in some cases obtained by chemically altering a substance which itself is made up of large molecules so that it acquires properties that make it useful as a plastic material. Examples of this are the conversion of cellulose to its esters and ethers, such as cellulose acetate, butyrate, and nitrate, and ethyl cellulose. In other cases the supermolecules are obtained by causing one or more base materials of low molecular weight to react chemically to form a material of high molecular weight. The

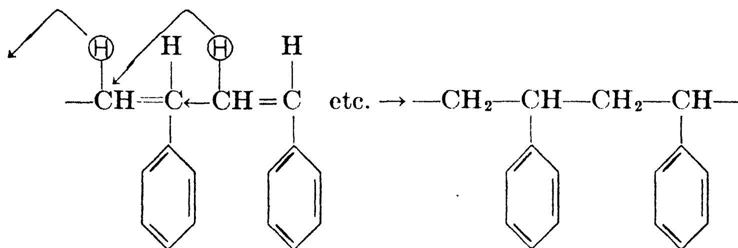
chemical change involved, which may take place either beforo or during the molding of the plastic, may be either a *condensation* or a *polymerization*.

Condensation.—In a condensation small molecules combine to form large ones with the elimination of another molecule, usually water. Thus, in the formation of Bakelite, molecules of phenol are chemically tied together by means of formaldehyde molecules:

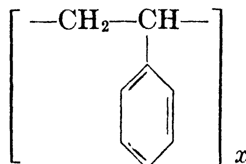


This process continues until a very large molecule is built. The changes shown are brought about by acidic or basic catalysts and heat.

Polymerization.—This process takes place by the addition of molecules of unsaturated compounds to one another in such a way that each addition involves the loss of one double bond. For example, the formation of polystyrene resin may be pictured:



to form a long chain which may be written:



The quantity in the bracket is called the *polymeric unit.* It is not necessary that all molecules involved in a polymerization be alike. Vinyl chloride and vinyl acetate react with each other to form a resin by the process illustrated for styrene. Such a resin is called a *copolymer*.

Types of Plastics.—Plastics are of two general types, *thermosetting*, those which set upon heating and cannot be reformed once they are set; and *thermoplastic*, those which become plastic when heated and which can therefore be reused. Table 84 shows, for several of the resins used in plastics today, the base materials from which the resin is made, its polymeric unit, process by which it is formed, and whether it forms thermosetting or thermoplastic plastics. The manner of setting depends upon the kind of resin used as binder. In general, those plastics containing a resin formed by condensation are thermosetting; those containing one formed by polymerization, as well as the cellulose plastics, are thermoplastic.

Fillers for Plastics.—As much as 50 per cent of a plastic may be a filler. Fillers serve two purposes, one of which is to reduce the cost per pound of the plastic. Their more important function, however, is to impart certain definite properties to the finished product. Thus barium salts have been used to produce a material impervious to X rays; inorganic fillers such as asbestos to increase resistance to heat and corrosive liquids; and shredded textiles to increase impact strength. Other materials used as fillers include wood flour, cotton, paper pulp, corn husks, graphite, carbon black, mica, clays, whiting, pumice, metallic oxides, and various metals such as iron, lead, copper, and aluminum.

Plasticizers.—These substances are added primarily to improve plasticity, thereby reducing the temperature and pressure required for molding. They also play a large part in determining the properties of the finished product and are chosen with this in mind. They may make up as much as 60 per cent of the plastic and are most often used with thermosetting plastics, particularly the cellulose derivatives. Cellulose acetate, for example, discolors when molded unless the molding temperature is reduced by the addition of a suitable plasticizer. A wide variety of organic materials find use as plasticizers. With cellulose acetate, some, such as camphor, increase surface hardness; others, such as tributyl phosphate and triphenyl phosphate, are used for flameproofing; and others, such as triacetin and tributyl phosphate, toughen the plastics. It is apparent that the development of the final composition of a plastic depends upon the use to be made of the material. It is a problem best solved by the plastics manufacturer who has a large amount of empirical data available.

Forming Articles from Plastics.—The methods of fabrication used for plastics include *casting*, *extrusion*, *molding*, and *lamination*,

TABLE 84.—SOME IMPORTANT CLASSES OF PLASTICS

Resin	Polymeric unit	Formed by	Thermosetting or thermoplastic
Phenol formaldehyde	$—C_6H_3(OH)—CH_2—$	Condensation	Thermosetting
Urea formaldehyde	$—NH—CO—NH—CH_2—$	Condensation	Thermosetting
Vinyl chloride-acetate	$—CH_2CHCl—CH_2CH(OCOCH_3)—$	Copolymerization	Thermoplastic
Methyl methacrylate	$—CH_2—C(CH_3)(COOCH_3)—$	Polymerization	Thermoplastic
Ethyl cellulose	$—C_6H_{10-n}O_5(CH_2CH_3)_n—$*	Chemical change of natural condensation material	Thermoplastic
Cellulose nitrate	$—C_6H_{10-n}O_5(NO_3)_n—$*	Chemical change of natural condensation material	Thermoplastic
Cellulose acetate	$—C_6H_{10-n}O_5(COCH_3)_n—$*	Chemical change of natural condensation material	Thermoplastic
Polystyrene	$—CH_2—CH(C_6H_5)—$	Polymerization	Thermoplastic

* n varies from 1 to 3.

sometimes followed by machining. *Laminated plastics* are usually made from sheets of paper, cloth, or even wood which have been impregnated with a suitable resin, usually a phenolic or urea type, piled on one another to give the desired thickness, and then heated and pressed together. In addition to laminated sheets, tubes and rods are also available. The final product, such as a gear, is made by machining blanks of the laminated plastic. Some progress has also been made in the compression molding of simple shapes from impregnated sheets. Laminated plastics have high tensile strengths and impact resistances. An important laminated material is resin-bonded plywood which can be used in the presence of water in place of ordinary wood with a decrease of about a third in weight and an increase of about a third in strength.

Casting refers to the forming of objects by pouring the liquid resin into a suitable mold. If phenolic resins are used, curing is accomplished by heating the resin in the mold for about 50 hr. at 175°F. and atmospheric pressure. Cast phenolics may be transparent or translucent, color well, and are now finding wide application. With thermoplastic resins such as methyl methacrylate the mold is filled with the monomeric form which then polymerizes in the mold at a temperature of about 110°F. under the influence of a suitable catalyst already added to the monomer.

The molding of plastics is done in a number of ways: *cold molding*, *compression molding*, *injection molding*, and *transfer molding*. Frequently the molding of the plastic is done around a metal insert so that the finished piece has a metal part firmly bonded to the plastic. The general procedures are as follows:

1. *Cold Molding.*—The object is formed in a mold by high pressure in the cold. It is then removed from the mold and baked to remove excess solvent and, in the case of phenolic resin compositions, to cause further condensation and hardening.

2. *Compression Molding.*—The raw materials are placed in a mold, and the mold carefully closed under low pressure. High pressure (500 to 5,000 psi) and moderate temperature (250 to 350°F.) are then applied to complete the curing of the resin. Compression molding is used primarily for thermosetting plastics.

3. *Injection Molding.*—The thermosplastic molding composition is warmed in a suitable chamber connected by a duct leading to the mold. The hot plastic is forced under a pressure of anywhere from 300 to 40,000 psi into the relatively cool mold where it is set by cooling, and the molded object is then ejected. Injection

temperatures range from 200 to 500°F.; the object when ejected has a temperature of about 125°F. Injection molding is used for thermoplastics.

4. *Transfer Molding.*—This is a variation of injection molding suitable for use with thermosetting plastics. The molding compound is plasticized by heat and pressure in a chamber outside of the mold and then injected into the mold where curing takes place under the influence of heat and pressure. More complicated shapes may be molded in this way than by ordinary compression molding.

Uses for Plastics.—The variety of uses made of plastics include housings for business machines, radios, electrical instruments, and telephones; timing gears; paneling for walls and instrument boards; decorative knobs for radios, automobiles, and various household appliances; lenses for goggles, lamps, and optical instruments; film tanks; closures for jars; tanks, kettles, pump parts, and vats for handling corrosive chemicals; translucent lamp globes; bearings; and equipment for textile plants. Of particular interest has been the development of nonmetallic bearings which have been found to last much longer than metallic bearings in some applications. These bearings are made from both laminated phenolics with canvas or paper base and molded phenolics with wood flour, fabric, or inorganic fillers. Graphite impregnation for lubrication is frequently used in both types. The bearings may be molded if there is a sufficiently large demand to warrant making a mold, or they may be machined from standard molded or laminated blanks. Lubrication can be effected by either grease or water. Water lubrication has made plastic bearings of particular value to industries, such as food industries, where there is a possibility of contamination from an oil-lubricated metallic bearing. Water-lubricated plastic bearings are also used extensively in rolling mills for steel where they have been found to be much superior to metal bearings.

Properties of Plastics.—In Tables 85 and 86 are listed the more important properties of several of the plastics in common use. Recalling that the kinds of fillers and plasticizers help determine the properties of plastics, it is easily understood that the examples given are merely illustrative of a few of the many plastics compositions available. The properties of the plastics are also dependent upon the time of cure, which determines the extent to which the polymerization or condensation reaction has progressed.

TABLE 85.—PROPERTIES OF PLASTICS

Type of plastic (molding unless otherwise indicated)	Specific gravity	Refractive index	Tensile strength, psi	Impact relative strength	Thermal conductivity*	Dielectric strength†	Dielectric k‡	Power factor‡
Phenol formaldehyde:								
No filler	1.28	....	6,000– 9,000	Low	....	400– 500	5–6	0.05–0.1
Wood-flour filler	1.25–1.50	....	6,000–11,000	Low	4–12	300– 500	5–12	0.04–0.3
Mineral filler	1.6–2.1	....	5,000–10,000	Low	8–20	250– 400	5–20	0.1–0.3
Fabric filler	1.4	....	6,500– 9,000	High	3–5	300– 450	5–10	0.08–0.3
Laminated paper	1.3	....	7,000–18,000	High	5–8	400–1,300		
Laminated cloth	1.35	....	10,000–14,000	Very high	5–8	150– 600		
Cast	1.3	1.5–1.7	5,000–12,000	Low	4	300– 450	5–10	0.025–0.20
Urea formaldehyde:								
Cellulose filler	1.48	1.55	8,000–13,000	Low	7–8	650– 720	7.6–8.6	0.04–0.055
Vinyl chloride-acetate	1.35	1.53	8,000–10,000	Medium	4–5	650		
Methyl methacrylate	1.18	1.49	4,000– 6,000	Low	4–7	500	3.5	0.05–0.06
Ethyl cellulose	1.14	1.47	7,000– 9,000	Medium	5–6	1,500	2.7	0.007
Cellulose acetate	1.3	1.48	3,500–10,000	High	5–8	350– 900	2.7	0.01–0.06
Cellulose nitrate	1.4	1.50	5,000–10,000	High	3–5	600–1,200	6.7–7.3	0.06–0.15
Polystyrene	1.06	1.59	5,000– 9,000	Low	2–4	500– 700	2.5–2.6	0.0001–0.0002

* 10^{-4} cal. per sec. per 1°C. per cm.
† In short-time volts per mil, 1/8 in. in thickness
‡ 60 cycles.

TABLE 86.—PROPERTIES OF PLASTICS

Type of plastic (molding unless otherwise indicated)	H_2O absorbed in 24 hr., %	Effect of sunlight	Effect of acids	Effect of alkalies	Light transmission	Colorability
Phenol formaldehyde						
No filler	0.01–0.02	Darkens	None unless acid is oxidizing	Decomposes	Transparent, translucent	Dark colors
Wood-flour filler	0.2–0.6	Discolors	None unless acid is oxidizing	Decomposes	Opaque	Limited
Mineral filler	0.01–0 03	Discolors	None unless acid is oxidizing	Decomposes	Opaque	Limited
Fabric filler	1.0–1.3	Discolors	None unless acid is oxidizing	Decomposes	Opaque	Limited
Laminated paper	0.3–9	Lowers surface resistance	None unless acid is oxidizing	Decomposes	Opaque	Limited
Laminated cloth	0 3–9	Lowers surface resistance	None unless acid is oxidizing	Decomposes	Opaque	Limited
Cast	0.01–0 5	Color may fade	None unless acid is oxidizing	Decomposes	Transparent, translucent, opaque	Unlimited
Urea formaldehyde-cellulose filler.	1–3	None	Decomposes	....	Translucent, opaque	Unlimited
Vinyl chloride-acetate	0.05–0 15	Darkens	Resistant	Resistant	Transparent, translucent, opaque	Unlimited
Methyl methacrylate	0 4–0 5	Very slight	Affected only by oxidizing acids	None	Transparent, 90–92% transmission	Unlimited
Ethyl cellulose	0.5–1 5	Slight	Decomposes	None	Transparent, translucent, opaque	Unlimited
Cellulose acetate	1.0–2.8	Slight	Decomposes	Decomposes	Translucent, transparent, opaque	Unlimited
Cellulose nitrate	0 6–2 0	Discolors, becomes brittle	Decomposes	Decomposes	Transparent, translucent, opaque	Unlimited
Polystyrene	0.00	Yellows slightly	None	None	Transparent, 89–90% transmission	Unlimited

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CHAPTER XVIII

RUBBER: NATURAL AND SYNTHETIC

By G. H. Stempel, Jr., Ph.D.

Natural rubber is an elastic material present in the latex of certain plants. The annual production of crude rubber is normally about 1,000,000 tons of which the United States consumes between 500,000 and 600,000 tons. More than 95 per cent of this rubber is obtained from the latex of rubber trees, *Hevea brasiliensis*, grown on plantations, mainly in Ceylon and the Malay Peninsula. Small quantities of rubber are produced in Brazil from uncultivated trees and from the *guayule* shrub in Mexico and southwestern United States.

Latex is a milky colloidal fluid containing from 30 to 45 per cent of rubber, the remainder being mainly water and a small amount of protein and resinous material. It oozes from superficial cuts in rubber trees and is collected in containers. A plantation-grown tree continues to yield for about 40 years and gives enough latex to make from 3 to 6 lb. of rubber each year. Latex is treated in two ways to obtain rubber goods. The crude rubber is either coagulated from it by acids or heat, and then processed; or the latex itself is mixed with appropriate compounding materials and then precipitated directly from solution in the shape to be used, such as a rubber glove. This latter treatment is new and important and will be discussed more fully later.

The recovery of rubber from guayule is carried out in a different manner. The entire plant, which may contain as much as 20 per cent by weight of rubber, is harvested after 4 years' growth, ground up, and soaked in water. The latex comes to the surface and is skimmed off; the woody material becomes waterlogged and sinks to the bottom. The resin content of guayule rubber is 18 to 20 per cent compared to about 4 per cent for hevea rubber. This resin may be extracted by means of solvents and can be recovered and utilized.

Crude rubber is usually obtained from latex by coagulation with organic acids, washing the coagulum well with water as it passes

between rolls, and finally drying the washed sheet as it comes from the rolls. If rough rolls rotating at different speeds are used and the rubber is then hung in the air to dry, the product is known as pale crepe rubber. If smooth rolls rotating at the same speed are used and the rubber is then dried in a smokehouse, the product is known as smoked sheets. It is tougher than pale crepe. Crude rubber is a tough, strong, elastic substance made up of 92 per cent or more of a hydrocarbon chain polymer $(C_5H_8)_n$. The polymeric unit appears to be: $—CH_2—CH{=}C(CH_3)—CH_2—$, from the hydrocarbon isoprene, $CH_2{=}CH—C(CH_3){=}CH_2$.

Crude rubber does not possess the properties that cause the familiar manufactured article to be considered so valuable. At the temperature of very hot summer weather, pure rubber becomes soft and sticky; during very cold weather, it becomes hard and brittle. In either of these conditions it is useless for the purposes to which it is commonly put. However, its properties are greatly improved by the addition of other materials followed by suitable heat or other treatment. Consequently, the manufacture of rubber articles involves some or all of the following operations:

Plasticization.—The crude rubber is "broken down" or plasticized, by passing it through rolls traveling toward each other at different speeds. This causes the rubber mass to be torn apart. The length of this treatment helps to determine some of the physical properties of the finished product, such as resistance to abrasion, which is decreased with increased breakdown.

Compounding.—To the plasticized rubber are added and mixed in by the rolls many other substances which may be classified as follows: (1) *Sulfur*, for vulcanization as described in the next section. (2) *Accelerators*, chemical substances that shorten the time required for vulcanization; their action is catalytic. These include such inorganic materials as lime, magnesia, litharge, and white lead. The organic accelerators, which are complex organic compounds, are more useful. Accelerators are added in the proportion of 0.5 to 1 part per 100 of rubber. Accelerator activators, of which ZnO is an example, are also added. In the presence of an accelerator, they further increase the rate of vulcanization although they have little activity alone. (3) *Antioxidants*, materials which in small quantities decrease the rate at which deterioration by air and light proceeds. These are essentially negative catalysts. They are complex organic compounds and are added in about the ratio of one part per 100 of rubber. (4) *Reinforcing agents*, such

as carbon black, zinc oxide, magnesium carbonate, barium sulfate, calcium carbonate, and certain clays. These strengthen and toughen the rubber and make up as much as 35 per cent of the rubber compound. (5) *Inert fillers*, added to lower the cost of the product, or to alter one or more of the physical properties of the mix in order to simplify manufacturing operations. (6) *Coloring agents*, including zinc sulfide (white), lithopone (white), titanium dioxide (white), lead chromate (yellow), ferric oxide (red), antimony sulfide (crimson), chromium trioxide (green), and ultramarine (blue). (7) *Plasticizers*, such as vegetable oils, paraffin oil, waxes, stearic acid, and rosin. (8) *Miscellaneous agents:* stiffeners to stiffen the stock until vulcanization has taken place; abrasives, such as silica and pumice; and many other materials occasionally added for some specific purpose.

Some typical compounding formulas are the following:

	Inner tube	Tire tread
Crepe	50	100
Smoked sheets	50	100
Sulfur	0.6	3
Organic accelerators	0.5	1
Organic activators	1.5	4
Zinc oxide	10	5
Soft black	40	
Carbon black	....	50
Antioxidant	1	1
Pine tar	....	3

Calendering.—If the rubber is to be made into sheets, it is passed through a calendering machine. The rubber compound passes between rolls which press it into sheets of uniform thickness varying from 0.003 to 0.1 in. Thicker sheets are made by rolling several thin sheets together. This avoids air pockets and other irregularities.

Vulcanization.—The rubber industry owes its existence to this process which was discovered by Charles Goodyear in 1839. It is carried out by heating the rubber compound containing sulfur. The sulfur combines chemically at the double bonds in the rubber molecule causing profound changes in its properties. Some of the more important of these are the following: the rubber is rendered much less sensitive to changes of temperature; it acquires increased

elasticity and tensile strength; it is more durable when exposed to the weather, and more resistant to the action of chemical reagents.

Vulcanization, or curing, as it is also called, may be carried out in several ways: the articles to be vulcanized may be heated with steam under pressure; they may be heated in air or in CO_2 gas; steam may be passed directly into the article, such as a fire hose; the article may be immersed in hot water under pressure; or the article may be vulcanized in the mold in which it is shaped. The temperature used is generally between 230 and 290°F. (110 and 140°C.). The time of cure, which varies from a few minutes to three hours, is important, overcured stock having decreased stretch and tensile strength; undercured stock is usually too soft, has excessive stretch, and lowered tensile strength. The amount of sulfur used varies from 1 to 5 parts per 100 parts of rubber for ordinary soft vulcanized rubber to 40 to 45 parts per 100 of rubber for hard rubber. Vulcanization can also be accomplished in the cold by either dipping the article in S_2Cl_2 or exposing it to the vapors of S_2Cl_2. This process, which was discovered by Parkes in 1846, is applicable only to very thin sheets of rubber.

The chief properties of vulcanized rubber which make it so valuable are its resiliency, low permanent set, resistance to abrasion, low electric and thermal conductivity, and resistance to the action of water, bases, and dilute acids. Rubber is attacked by oxygen in the air and by sunlight. As has been mentioned, the rate at which these changes proceed can be greatly reduced by the addition of antioxidants. Concentrated acids react with rubber and destroy it. It is soluble in such solvents as benzene, petroleum ether, gasoline and other petroleum derivatives, carbon tetrachloride, carbon bisulfide, and turpentine. Rubber, being a true colloid, does not dissolve sharply as do salts in water. The solvent is first absorbed by the rubber, which swells and forms a jellylike mass. In a sense the solvent may be said to have dissolved in the rubber. Finally, when enough of the solvent has been absorbed, the mass assumes the liquid state. Solutions of rubber in benzene are used as adhesives.

Reclaimed Rubber.—It is possible to recover or reclaim rubber in a usable condition from worn-out articles and rubber waste from the factories. Although usable, it must not be understood that it has been devulcanized and returned to the condition of virgin rubber, for to the present time, no one has been able to accomplish this very desirable result.

There are several processes by which rubber may be reclaimed but that which is most widely used is known as the *alkali process*. In this process, the rubber, after having been separated from the metal and fiber as much as possible, is heated in a closed iron vessel with an aqueous solution of an alkali, generally sodium hydroxide. This treatment removes the remainder of the fabric, and all the free sulfur as an alkaline sulfide. The rubber thus treated is then carefully washed and dried and may be incorporated with a compound of fresh rubber.

Reclaimed rubber is sometimes known as "rubber shoddy." In general, it possesses much lower tensile strength, elasticity, and wearing power than new rubber. Nevertheless, some of it is of extremely good quality and sometimes it may be superior to some of the poorer grades of crude rubber. Its value seems to be to a certain extent dependent upon the degree to which the reclaiming process has regenerated its plasticity, but in any event, because the old rubber has already been largely oxidized, its use with the fresh rubber is said to make a product that is less susceptible to oxidation than one containing all new rubber would be. On the other hand, the elasticity of such mixtures must be in the same measure sacrificed.

Rubber Goods Directly from Latex.—The manufacture of rubber goods directly from latex is a recent development that is advancing rapidly. It has several advantages: it does away with expensive machinery; the rubber is not masticated or broken down, and has, therefore, a higher tensile strength; and vulcanization can be effected more rapidly. The compounding of latex is much the same as that of precipitated rubber, except that inorganic reagents produce no reinforcement when added to latex. All dry ingredients must first be emulsified in water before adding to the latex; otherwise they coagulate the latex. The latex compound is used in a variety of ways to make the finished articles. Some are made by dipping forms into the latex compound; insulated wire is made by passing wire through the compound; cord and fabric are impregnated with rubber by dipping; rubber thread is made by extruding latex into a coagulating bath; and sponge rubbers are made by whipping air into the latex compound mechanically, and then adding a coagulant. In all cases, the forming process is followed by vulcanization.

Synthetic Rubbers (Elastomers)

One of the most interesting developments in the rubber industry is that of synthetic rubbers, or *elastomers*, which are derived from

such raw materials as coke, limestone, petroleum, natural gas, salt, alcohol, sulfur, ammonia, and coal tar. Elastomers are not, strictly speaking, synthetic rubber, for rubber has never been synthesized. They are rubberlike materials which have many of the characteristic properties of rubber and some of which resemble rubber in their chemical structure.

Elastomers are rapidly increasing in importance. They serve as potential sources of rubber, independent of rubber plantations. Construction of plants in the United States with an annual production capacity of nearly 1,000,000 tons, to be completed by the end of 1943, has been authorized. The cost of producing many of the elastomers approximates that of natural rubber. In view of these facts and of the precarious position of the rubber plantations in the war zone, it would appear probable that synthetic rubber may displace the natural product even in normal times.

The processing of synthetic rubbers involves approximately the same steps and equipment as that of crude rubber. Their properties, while similar to those of rubber, are capable of wider variation. For example, as seen in Table 88, some elastomers are more resistant than rubber to sunlight; others have greater solvent resistance; and some have greater elasticity. In the future it will, in many cases, be possible to choose a synthetic rubber to fit a given application, rather than adjusting the application to the properties of the rubber.

In Table 87 are listed some of the more important elastomers along with their typical polymeric units (page 530). Although some

TABLE 87.—SOME COMMON ELASTOMERS

Elastomer	Raw materials derived from	Polymeric unit
Buna 85	Petroleum or alcohol	$—CH_2—CH{=}CH—CH_2—$
Buna S	Petroleum or alcohol, coal	$—CH_2—CH(C_6H_5)—CH_2—CH{=}CH—CH_2—$
Perbunan	Petroleum or alcohol, coal, ammonia, salt	$—CH_2—CH(CN)—CH_2—CH{=}CH—CH_2—$
Vistanex	Petroleum	$—CH_2—C(CH_3)_2—$
Neoprene	Coal, lime, salt	$—CH_2—CCl{=}CH—CH_2—$
Thiokol	Petroleum or natural gas, sulfur, salt	$—CH_2—CH_2—S_x-$
Butyl rubber	Petroleum	$—CH_2—CH{=}CH—CH_2—CH_2—C(CH_3)_2—$
Koroseal*	Petroleum or natural gas	$—CH_2—CHCl—$

* Highly plasticized, mainly with tricresyl phosphate.

are merely polymers of a given molecule, others are copolymers formed by the joining together of different molecules. In fact, it

would appear that the most fruitful field of investigation of elastomers lies in the development of other copolymers, since there is a greater probability of varying specific properties by copolymerization than by simple polymerization involving only one kind of molecule. Of the elastomers listed in the table all are improved by vulcanization except Vistanex and Koroseal; these have no double bonds left in their polymeric forms and do not vulcanize.

In Table 88 are listed some properties of rubber and some of the more important elastomers.

TABLE 88.—SOME PROPERTIES OF RUBBER AND ELASTOMERS

Elastomer	Density (Unvulcanized)	Vulcanized carbon black compound					
		Effect of sunlight	Tensile strength, psi	Elongation, %	Resistance to swelling by		
					Gasoline	CCl_4	Benzene
Natural rubber.....	0.911	Deteriorates	5,000	650	Poor	Poor	Poor
Buna 85...........	0.92	Deteriorates	2,490	600			
Buna S............	0.91	Slight	4,200	650	....	Poor	Poor
Perbunan	0.96	Slight	5,000	600	Good	Poor	Poor
Chemigum*........	.....	Deteriorates	4,425	630	Excellent	....	Poor
Hycar OR*... ...	1.00	Deteriorates	3,500	450	Excellent	Fair	Poor
Vistanex HM†......	0.913	Slight	855	1,000	Poor	Poor	Poor
Neoprene..........	1.25	Slight	4,125	760	Good	Poor	Poor
Thiokol A..........	1.60	Slight	855	370	Excellent	Excellent	Good
Thiokol D	1.34	Slight	1,705	610	Excellent	Fair	Poor
Butyl rubber... ...	0.91	Slight	3,600	600	Poor		

* Chemigum and Hycar OR are copolymers of butadiene with other substances as yet not made public.

† Not vulcanized, uncompounded.

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CHAPTER XIX

ORGANIC PROTECTIVE COATINGS

PAINTS, VARNISHES, ENAMELS, LACQUERS

By K. K. Stevens and J. C. Warner

This chapter includes a rather brief description of the above products, with the raw materials used in their manufacture. The purpose of organic coatings is either protective or decorative, or both. They are applied to various materials of construction, by brushing, spraying, or dipping, forming a smooth even coating of the desired thickness which is usually, for the outer layer, about 0.001 to 0.003 in., varying considerably according to the method of application. These products, although basically the same as 30 years ago, have been considerably modified and improved by research, so that they are much more satisfactory than those formerly on the market. This is especially noticeable in varnishes. Lacquers were very crudely formulated until about 1920. Forty or fifty years ago paints were not required to meet the rigid specifications imposed today; atmospheric conditions were less strenuous, and the types of materials painted were less varied. At present all the large manufacturers of paints, varnishes, and lacquers maintain research laboratories and new or improved products are of daily occurrence.

Paints.—As usually defined, *paint* is a dispersion of pigments in a drying oil, with the addition of driers and thinners, the former to accelerate film formation and hardening, the latter to allow ease and uniformity in brushing or spraying. The function of the pigment is to give the desired color and to prevent to a great extent the decomposition of the film by ultraviolet light. It also gives more impervious products. Another important factor is the ratio of pigment to vehicle, which is determined largely by the bulking value (page 549) of the pigment and is in turn dependent upon the specific gravity. For example, basic lead carbonate (sp. gr. of 6.7) has low bulking value, about 55 lb. per gal., and mixes easily with the oil. With some other pigments more oil is required per

gallon of paint. In recent years a small percentage of varnish has been added to some paints to give a harder and more durable finish tending toward an enamel.

Strictly speaking, the above are "oil" paints as distinguished from pigments dispersed in water or other vehicle, but usage has given the term "paint" to the above. All others are designated by the vehicle, such as *cold water paints*, or *distempers* if suspended in albumin. *Calcimines, casein paints, rubber paints,* and others have little in common with "oil" paints except perhaps the pigments used.

Film Formation in Paint.—In the description to follow on pigments and vehicles (oils and resins), reference will be made to characteristics of the different materials causing various effects in the paint film, and it seems advisable to describe the formation of a film, with some of its desirable characteristics, so that they will be understood when mentioned later.

If the solvent of a solution is removed by evaporation, a film of solute is left. In the case of salt solutions, the residue is merely a dry powder and is easily removed; if it happens to be a sugar solution, a sirupy residue is first left, similar to a paint film, but the film is not at all firm and becomes crystalline on further evaporation. With a drying oil, dissolved in a thinner such as turpentine and omitting the pigment which has little to do with the initial film formation, the thinner evaporates leaving a thin film of oil on the surface. This oil, which in paints and varnishes must consist to a considerable extent of unsaturated glycerides, becomes saturated by combining with oxygen from the air forming a film more or less hard, which in time loses its stickiness and results in a fairly firm homogeneous coat. This oxidation is characteristic of drying oils, *i.e.*, unsaturated oils, and the resulting coat is more or less firm and durable depending mostly on the degree of unsaturation of the oil used. Since the oxidation is quite slow, "driers," which are usually lead, manganese, or cobalt compounds, may be added to accelerate the process.

From a strictly physicochemical viewpoint, the theory is that the oil, taking up oxygen, forms peroxide linkages in the molecule, volatile oxidation products are split off, increasing the polarity of the molecules, which become larger by combining with other molecules, and a gel is formed. This gel becomes gradually harder by action of light and air; if the aging is long enough, it becomes brittle and eventually disintegrates. It is at this stage that the function

of the pigment, in shutting out most of the ultraviolet light, protects the film thereby giving it longer life. Naturally this depends upon the type or types of pigments used, since some are more pervious than others. A single pigment consisting of equally sized particles leaves more voids than a mixture of pigments having different sized particles. The latter not only shut out the light more effectively, but also add tensile strength to the film. The darker the pigment, the less light is admitted and, other things being equal, the more durable is the film.

Varnishes.—These materials differ from paints mainly in the resin incorporated with the oil at an elevated temperature with the result that upon evaporation of the thinner the film remaining is reinforced by a firm substance thoroughly incorporated with the oil. The nature of the resulting film is due to the characteristics of the oil, as in paint, and to those of the resin used. It is usually much harder and more impervious to moisture than a paint film, but it is not protected from light. For this reason varnishes are used mostly where a natural wood finish is desired, and where the film is not exposed to ultraviolet light. In the manufacture of varnishes the oil-resin ratio is important, as is the oil-pigment ratio in paints. The more oil, the more elastic and more durable the film, with a sacrifice of hardness and air-drying speed. This ratio is designated as "gallons of oil per hundred pounds of resin." Synthetic resin manufacturers have formulated stock solutions which may be cold blended to give any type of varnish desired.

Enamels.—When a varnish finish is to be exposed to sunlight, it is colored by pigments and is called a "brushing enamel." If this coating is on metal and is properly formulated, it may be subjected to higher temperatures and is then termed "baking enamel." This should not be confused with "vitreous enamels" which are inorganic in composition (page 461).

Lacquers (Pyroxylin Varnish).—Lacquer and varnish coats are similar in appearance, but are quite different in composition. Lacquer coatings developed from *spirit varnishes* which were merely solutions of resin in a volatile solvent and the coatings were quite brittle and short lived. The only surviving spirit varnish today is shellac which is lac resin dissolved in alcohol; it has individual properties possessed by no other coating. Originally lacquer was used mainly as a decorative coating for small objects and never in exterior coatings.

At the close of the war of 1914–1918, the solvent and cellulose manufacturers had no outlet for their products and finally hit upon the idea of lacquer manufacture for exterior coatings, for automobiles and motor boats. Development of spray painting was largely responsible for this type of coating. This lacquer was a solution of nitrocellulose (pyroxylin), with some resin, in a suitable solvent. The resulting coatings were good looking but were sadly lacking in adherence and durability. These defects were gradually remedied; the adherence was increased by the addition of suitable gums or resins, and the durability and flexibility were improved by substances that were merely solvents of low volatility called "plasticizers." Nitrocellulose or cellulose nitrate is manufactured in several grades differing in viscosity when the same amount is dissolved in the same volume of solvent. This varies from ½ to 200 sec. as determined in a specially designed apparatus called the "falling ball" viscosimeter. The original lacquer cellulose was so viscous that a solution containing only 4 lb. per gal. could not be sprayed. The important advantage in the use of lacquers instead of varnishes consisted mainly in the speed of application, and the cellulose nitrate manufacturers soon devised methods for producing cellulose esters of any desired viscosity.

One disadvantage of the low-viscosity cellulose is that it produces a weak film, and must be reinforced by increased resin content. A few years ago the ratio of cellulose derivative to resin was 3:1. Today it is almost reversed. With some 284 plasticizers, 260 synthetic resins, and 156 solvents to select from at the present writing, it can be seen that lacquers with almost any desired property can be produced.

Lacquer, as first produced, was called collodion, a solution of the cellulose ester in an ether-alcohol solvent, and was used in covering cuts and burns. Today it is used in nail polish, cellophane coatings, cement, leather dopes, and many other products.

Lacquer Enamels.—Like varnishes and enamels, lacquer enamels are merely clear lacquers plus pigment, the object being to cover as much area as possible with a firm, colored, permanent film at the lowest cost. The cheaper varieties, used on toys and other articles of short life, are made using less cellulose ester of high viscosity, cheaper solvents, coarser pigments, and sometimes scrap film. The pigment is incorporated by grinding it in some oil, usually castor oil, then grinding it with the lacquer. The ball mill is very

satisfactory for this purpose, and recently high-speed colloid mills have come into use.

One problem in the manufacture and use of lacquer enamels is that of adhesion. The presence of large amounts of pigment reduces the adherence and gives a more brittle film than the same lacquer base would possess. Since this adhesion varies with the type of surface, the problem becomes quite complicated, each type of surface requiring a specially prepared enamel to obtain the best results. Wood, brass, and some steels are not difficult to coat, but aluminum and tin may require priming and several finishing coats. A glossy finish is usually obtained by using a clear finishing lacquer over the colored lacquer enamels, for colors other than red and black.

Red and black lacquer enamels are in great demand as one-coat gloss enamels, but are rarely used as flats. Hardness is probably the most important property required in a lacquer enamel, with flexibility second. If the coated material is to be subjected to bending, the proper use of plasticizers is of vital importance, especially in pigmented lacquers where the film is more brittle. Increasing the amount of plasticizer in a lacquer usually increases the drying time and makes the film more flexible and softer. An enameled steel plate should stand impacts of a ball-peen hammer making dents ⅛ to ¼ in. in depth without cracking. It must also be remembered that lacquer grows more brittle as it ages.

RAW MATERIALS

The raw materials used in the production of paints, varnishes, enamels, and other special coatings may be subdivided into pigments, oils, driers, solvents and diluents, resins, and cellulose derivatives.

Pigments

Used originally in paints and enamels for color and hiding power to cover the original surface so that grain and defects were hidden, it is recognized today that the function of the pigment in reinforcing the film mechanically and in preventing the penetration of ultraviolet light is as important, if not more so, than the color and hiding power. Other factors being equal, the life of the film is largely dependent upon the depth of color. The use of composite pigments instead of a simple pigment is also an important factor in giving greater durability because a range of particle size allows fewer voids

with a consequent lower porosity and greater strength for the film. For example, it was established from experiments conducted in 1910 by the National Paint Manufacturers' Association that a pigment composed of 60 per cent of white lead, 30 per cent of zinc oxide, and 10 per cent of "inerts" such as barytes, silica, of asbestine was a more efficient combination for outside paints than white lead alone.

Some of the important properties of pigments, aside from color are the following: The *bulking value* represents the volume occupied by the pigment in the finished product. This usually is expressed in gallons occupied per pound of pigment, or as the reciprocal, pounds of pigment occupying a volume of one gallon in the product. To calculate bulking value the true specific gravity or density of the pigment must be known. The *hiding power* of a pigment may be determined by standard tests,[1] and depends upon the difference between the refractive index of the pigment and the refractive index of the oil or other film-forming substance in the protective coating. The *oil absorption* characteristics are important since they determine the amount of oil needed to grind the pigment to a satisfactory paste. This characteristic[2] is usually expressed in pounds of oil needed per 100 lb. of pigment. This property depends upon the oil used as a vehicle, the particle size distribution in the pigment, and the interfacial tensions between pigment-oil, pigment-air, and possibly between pigment-water. White lead, for example, is wetted so strongly by linseed oil that a white lead-oil paste may be prepared by grinding water-bearing white lead with oil.

As has been mentioned, the *particle size distribution* in a pigment is an important factor in determining the oil-absorption characteristics of a pigment and the mechanical strength and life of paint, enamel, and lacquer-enamel films. A number of standard methods for determining particle size distribution are available.[3] Most pigments contain only a few tenths of a per cent or less of particles large enough to be retained on a 325-mesh screen. Most pigments have particles that average 0.1 to 5.0 microns[4] in diameter. Any tendency of the pigment to react with the film-forming oils and

[1] GARDNER, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," 9th ed., pp. 9–29, Institute of Paint and Varnish Research, Washington D. C., (1939). Hereafter referred to as Gardner, 9th ed.

[2] GARDNER, 9th ed., pp. 200–215.

[3] GARDNER, 9th ed., pp. 186–199.

[4] 1 micron = 0.0001 cm.

resins in a product, or with constituents of the atmosphere, should be carefully noted. Their influence upon the aging characteristics of a film is likewise important.

White Pigments.—Excluding "extenders," or "reinforcing pigments" (page 552), which are usually whites, the principal white pigments are white leads, sublimed white leads, zinc oxides, lithopones, and titanium dioxide. The inorganic solids in many white commercial products frequently consist of mixtures in various proportions of the above whites along with a certain percentage of inerts, extenders, or reinforcing materials.

White lead is a basic lead carbonate of somewhat variable composition. It may be approximately represented by the formula $(PbCO_3)_2 \cdot Pb(OH)_2$. This is one of the oldest pigments in use and is made by at least five different processes:[1] Old Dutch, Carter, French, Rowley, and Sperry electrolytic.

White lead possesses good hiding power and mixes very readily with oil to form a smooth paste. Although white lead reacts to some extent with linseed oil, the reaction is not sufficient to give a hard brittle film such as is characteristic of some pigments; with white lead as pigment, the vehicle film is tough and elastic. The use of white lead alone is not to be recommended any more than is the use of any single pigment. It tends to produce incipient chalking, with a slight roughening of the surface, causing the adherence of soot and dust particles that leave an unattractive coating. The darkening of coatings containing white lead in industrial atmospheres has been attributed by some to the conversion of lead carbonate to black lead sulfide.



$$PbCO_3 \text{ (white)} + H_2S = PbS \text{ (black)} + H_2O + CO_2$$

The resistance of basic lead sulfate to darkening in similar atmospheres has been attributed to the fact that the lead is already combined as sulfate; the fact that part of the lead in basic sulfate is present as $Pb(OH)_2$ seems to have been overlooked.

In an investigation[2] sponsored by the National Association of Paint Manufacturers, one of the authors had the opportunity to

[1] Riegel, "Industrial Chemistry," 3d ed., pp. 539–544, Reinhold Publishing Corporation, New York (1937). Mantell, "Industrial Electrochemistry," 2d ed., McGraw-Hill Book Company, Inc., New York (1940).

[2] Mellon Institute of Industrial Research, "Smoke Investigation," *Bull.* 6 (1913), Pittsburgh, Pa.

study the darkening of white outside paints in industrial atmospheres. This investigation showed that paints containing white lead pigments darkened, but that the discoloration was due to the deposition of soot and other carbonaceous material in the more or less porous film. No sulfides were found in the film, and the film thickness was not much decreased during the exposure period. The most notable change in the films containing white lead was conversion of carbonate to sulfate.

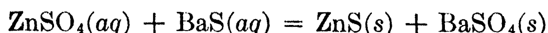
In this same investigation, paints containing basic lead sulfate did not darken, but these coats decreased in thickness during exposure, showing chalking, and it seems justifiable to infer that they did not darken, because deposited soot and dust were washed away by rain.

That the darkening of outside paints containing lead compounds as pigments is *not* due to lead sulfide formation is in agreement with our knowledge that hydrogen sulfide evolved into industrial atmospheres is quite rapidly oxidized to sulfur dioxide and sulfuric acid. It would, therefore, seem that lead pigments would not be darkened because of the formation of lead sulfide unless the source of hydrogen sulfide was near the paint coating, a situation that might be encountered in the chemical laboratory or in certain industrial plants, but rarely in outdoor exposure.

Sublimed white lead is a basic lead sulfate, having the approximate composition $(PbSO_4)_2{\cdot}Pb(OH)_2$, made by roasting galena, then oxidizing the volatilized lead sulfide in an air blast, and collecting the cooled finely divided product in bags. If the product is darkened by the presence of finely divided lead, it is called *sublimed blue lead.*

Titanium whites are the newest white pigments. They range all the way from fairly pure titanium dioxide to mixtures containing as little as 25 per cent of titanium dioxide mixed with barium sulfate, calcium sulfate, magnesium silicate, zinc oxide, or other white pigments. Most titanium dioxide is made from ilmenite, $FeO{\cdot}TiO_2$, by solution in sulfuric acid, precipitation of the hydrated titanium dioxide, and calcination to expel the combined water. Due to the high refractive index of titanium dioxide, these pigments possess excellent hiding power and are widely used in all sorts of exterior and interior organic coatings. Titanium whites impart excellent properties to coatings by mechanically reinforcing and increasing the life of the film.

Lithopone is made by the coprecipitation of insoluble barium sulfate and zinc sulfide by mixing solutions of barium sulfide and zinc sulfate under carefully controlled conditions.



$$ZnSO_4(aq) + BaS(aq) = ZnS(s) + BaSO_4(s)$$

The precipitate usually contains 70 to 75 per cent of barium sulfate, the remainder being zinc sulfide.

Zinc oxide for use as a pigment is produced in a variety of ways but almost all of them involve the controlled oxidation of relatively pure zinc vapor (page 169). Zinc oxide is extremely effective in excluding ultraviolet light from paint or enamel films.

Reinforcing Pigments.—In relatively small amounts, the pigments grouped under this head are useful in overcoming the defects of other pigments, but they should never be used in excess. They may be divided into two classes: (1) those that grind in oil to produce a white paste, and (2) those that are practically transparent in oil. The former dilute other colors to produce a lighter tint and hence are called *diluents*. Those that do not produce white pastes, due to the fact that they have about the same refractive index as oil, will, when used with colored pigments, allow the full strength of the colored pigment to be effective. Reinforcing pigments of this type are called *bases*.

The chief *diluents* are asbestine, talc, and china clay; the principal *bases* are silica, natural and precipitated calcium carbonate, gypsum, and natural and precipitated barium sulfate.

Blue Pigments.—One of the chief blue pigments is *Prussian blue*, $Fe_4[Fe(CN)_6]_3$, which also has such names as *Paris blue*, *Chinese blue*, and *milori blue*. This pigment is made in a variety of slightly different ways, the depth of color varying somewhat with the method. In the usual method, it is made by treating freshly prepared aqueous solutions of ferrous sulfate with solutions of potassium ferrocyanide. A white or greenish-white precipitate of ferrous ferrocyanide is formed, which is oxidized with a reagent such as bleaching powder to the ferric ferrocyanide (Prussian blue). The coloring power of this pigment is very great. It is one of the best blues in this respect; ½ oz. will tint 20 lb. of zinc white a perceptible blue. It is quite permanent, resists the action of atmospheric agencies and light, absorbs much linseed oil which it tends to preserve, and presents a glossy surface even after long exposure. Prussian blue cannot be used with whiting, basic carbonate white lead, or other basic pigments because it reacts with

them to precipitate ferric hydroxide which imparts a reddish tinge to the mixture.

Another blue pigment is *ultramarine*, a complex sodium aluminum silicate and sulfide which occurs in nature as the mineral *lapis lazuli*. The pigment may be made by fusing together clay, sodium sulfate, and carbon. A portion of the sulfate may be replaced by carbonate. Depending upon the process of manufacture, the color may range from a pale greenish blue to a violet blue. It is much used as a laundry blue and for neutralizing yellow tones in fabrics, starch, and paper. It is stable toward alkalies but evolves hydrogen sulfide in contact with acids. Although ultramarine is a satisfactory pigment for painting on wood, it is not a good pigment for painting on iron because of its sulfide content. It should not be used with such pigments as white lead and chrome yellow because of the darkening that results from the lead sulfide formed.

Other blue pigments are *copper phthalocyanine* and *cobalt blue*, the latter usually containing about 30 to 35 per cent of Co_3O_4 and 65 to 70 per cent of Al_2O_3.

Green Pigments.—The green pigments may be divided into two classes: (1) those having an inherent or natural green color, and (2) those prepared by an intimate mixture of blues and yellows.

The most important green pigment of the first class is *chromium oxide*, Cr_2O_3, also known as *permanent green* or *Guignet's green*. It is brilliant dark green in color and possesses unequaled permanence. It is not affected by atmospheric agencies and light, nor, if pure, by acids or alkalies. It does not interact with other pigments, has good body, good covering power, and possesses inhibitive properties when used in paints for metal surfaces. It frequently is mixed with chrome yellow but the mixed pigment will not withstand acids and cannot be used above 300°F., whereas the pure chromium oxide is resistant to temperatures as high as 800°F. The chief handicap of chromium oxide as a pigment is its high cost.

The more widely used green pigment, *chrome green* (also called *Brunswick green*, *Prussian green*, or *green vermilion*), consists of an intimate mixture of Prussian blue and lead chromate (*chrome yellow*). It can be made by grinding together these two colors, but it is more often prepared by precipitating these two colors on barium sulfate or lead sulfate. By varying the relative amounts of chrome yellow, Prussian blue, and white pigments, a great

variety of shades and tones of green may be obtained. The chrome greens have better covering power than any other green pigments. They are not recommended as pigments for primer coats on iron. They should not be used with pigments containing sulfide sulfur, nor with basic pigments such as basic carbonate white lead or whiting. Chrome greens cannot be used with acids, which dissolve the chrome yellow and cause the green to change to blue.

The *Paris greens* (*emerald green* or *Schweinfurt green*) are used to a limited extent as green pigments. These greens are copper acetoarsenites or -arsenates.

Yellow Pigments.—The chief yellow pigments are chrome yellow, zinc chrome, yellow ocher, orange siennas, and cadmium yellows.

The *chrome yellows* contain lead chromate, $PbCrO_4$, as their chief constituent, made by precipitation from a solution of a soluble lead salt with a solution of a dichromate. Depending upon the shade desired, however, the pigment may contain lead sulfate (which may be precipitated simultaneously with the chromate by the addition of sulfuric acid or other soluble sulfates), gypsum, china clay, barytes, lead oxide (to produce a basic lead chromate), molybdate, or other insoluble lead salts. The lighter shades of chrome yellow may contain as much as 60 per cent of white pigment. The chrome yellows are very brilliant and have the greatest covering power of all the yellow pigments. They are unaffected by light, but are darkened by sulfide sulfur and are turned orange by basic pigments such as basic carbonate white lead. The chrome yellows have been recommended in the past as inhibitive pigments for primer coats on metals; recent evidence, however, indicates that they are rather inert in this respect, neither accelerating nor inhibiting the corrosion of iron or steel.

Zinc chrome (*citron yellow*), $ZnCrO_4$, is prepared by precipitating the pigment from zinc salt solutions by soluble dichromates, or by boiling zinc oxide with solutions of sulfuric acid and dichromates. This pigment has good covering power, is a delicate bright sulfur yellow in color, is not affected by light, constituents of the atmosphere, hydrogen sulfide, or other pigments, but is attacked by acids Tests conducted some years ago by the Paint Manufacturers' Association, as well as recent tests, show that zinc chromate is definitely an inhibitive pigment when used in paints to be applied to iron or steel. The usual recommendation is that 2 per cent of this pigment be added to paints for this purpose.

Yellow ochers are natural pigments found in many localities; they consist of either clay or calcium carbonate, colored with about 20 per cent of hydrated ferric oxide. They are prepared for use by grinding and levigating; the latter process allows the coarser particles to settle out and carries the desired fine particles into a settling tank. The fine particles, after drying, are ready for use as a pigment. Ochers may be given a reddish tone by calcination to partly dehydrate the ferric oxide. The uncalcined ochers usually have a golden-yellow color, moderate opacity and spreading power, and they are not affected by other pigments or the constituents of the atmosphere.

In addition to the above, *cadmium yellow*, CdS, either alone or mixed with whites such as barytes or zinc oxide, is a minor yellow pigment. The natural *siennas*, upon calcination, usually are brown or dark red; some, however, are reddish orange in color. The siennas, in general, possess low opacifying power and may be used in thin overcoats (*glazes*) to modify the tone of another pigment. Litharge, PbO, also finds some use as a yellow pigment.

Red Pigments.—Red lead, prepared iron oxides, naturally occurring iron oxides, cadmium reds, and chrome reds are the principal pigments of this class.

Red lead (minium), Pb_3O_4, is prepared by heating metallic lead in furnaces in the presence of air, whereby litharge, PbO, is formed. Litharge is then further oxidized to red lead by heating in muffle furnaces to about 375°C. (710°F.). This bright red pigment is unaffected by light but cannot be used with pigments or atmospheres containing sulfide sulfur. It requires less oil for making a paste than most pigments and has a pronounced effect in accelerating the rate of drying of oil vehicles. For this reason driers are unnecessary in red lead paints; indeed to overcome this accelerating effect somewhat, red lead usually is mixed with inert materials when used as a pigment. Red lead shows decided inhibitive properties when used as a pigment in paints for iron and steel, and for this reason finds extensive use in primer coats for steel structures.

Venetian red consists of a mixture of ferric oxide, Fe_2O_3, and calcium sulfate, $CaSO_4$. It is prepared by heating a mixture of ferrous sulfate, $FeSO_4$, and quicklime, CaO. The amount of calcium sulfate varies, but may make up as much as half of the mixture. The color of the pigment depends somewhat upon the temperature of the furnace; the lower temperatures produce the brighter colors.

Venetian red is a very permanent red pigment. It does not affect other pigments nor is it affected by them. It forms excellent protective paints for wood, is especially good as a priming coat, but is not a good paint for metal. The calcium sulfate, which it contains, dissolves and ionizes slightly in water; the resulting sulfate ions are active in stimulating corrosion. Also it may contain some sulfur trioxide not properly neutralized by lime during the calcination. It does not exert a drying action on the oil as does the red lead, and the longer it stands in the full amount of oil it is to receive, the better paint films it seems to produce.

Natural Iron Oxides (Indian Red, Colcothar).—These iron-oxide pigments are obtained by grinding red hematite iron ores, levigating with water, and then drying. Although they vary much in composition, they contain usually from 88 to 95 per cent of iron oxide and the remainder clay and silica.

Their properties are very similar to those of the Venetian reds; for metals the natural oxides are much better, since they contain no ionizing calcium sulfate nor any free acid.

Chrome Red (American Vermilion, Basic Lead Chromate), $Pb_2(OH)_2CrO_4$.—This is the most highly basic of the lead-chromate pigments. It is obtained by boiling white lead with a solution of potassium dichromate and then treating the mass with a small quantity of sulfuric acid to brighten the shade.

Its particles are granular and coarse. Its general properties resemble those of chrome yellow. For painting on metal it has very excellent inhibiting powers; it is among the best of pigments for this purpose.

Brown Pigments.—Practically all the important brown pigments contain iron oxides as the color-giving constituent. They may be made from various ferrous materials, usually by-products of other processes, or may be produced by the treatment of natural minerals such as the umbers and some of the siennas.

Prince's Metallic Brown (Prince's Mineral).—This is an oxide of iron pigment mined as an ore. It occurs both as the hydrated oxide and as the carbonate, which are roasted at a red heat and then are ground. The pigment contains a high percentage of alumina and silica.

It has a good brown color and is very permanent. Its particles are generally fine but of varying sizes. It forms compact paint coats that are very good for both wood and metal.

Umber is also a natural pigment consisting of a clay base containing iron oxide. It belongs to the same general class as the ochers but differs from them in that it contains considerable amounts of the brown manganic oxide. The raw umber is of a dull grayish-brown color, but upon burning (calcining) it turns to a reddish-brown, which color is very permanent. Its properties in general very much resemble the properties of the ochers.

Vandyke brown consists of a mixture of red iron oxide and yellow ocher, darkened with lampblack or some bituminous compound. It is very permanent upon exposure, and works well in oil, but it seems to cause the paint to dry poorly.

Black Pigments.—*Lampblack* is made by burning heavy refuse oils in a limited supply of air. It is in reality a soot, averaging about 98 per cent pure carbon. There are various grades. The soot from the flame is received into different chambers arranged in a series. The black that collects in the first chamber contains a certain amount of oily matter which has passed off unburned. On this account it has a brownish or grayish tint. That in the farther chambers is freer from the oily deposit. Lampblack in general possesses a grayer tone than many of the other carbon pigments so that it may often be recognized by this fact. Lettering made with lampblack will appear light on a background painted with ivory black or drop black.

Its particles are very fine and uniform. It is very permanent and seems to preserve the oil with which it is mixed, thereby producing very permanent paints. It outlasts lead and zinc paints for wood. It has a specific gravity of 1.82 and grinds in 75 per cent of oil to a stiff paste. It retards drying. This property may be due to the effect of the hydrocarbon oil it contains. Toch says that less than 1 per cent of unburned oil will retard the drying to such an extent as to render the pigment unfit for use.

Carbon Black (*Gas Black*).—This pigment also contains about 98 to 99 per cent pure carbon and is obtained by burning hydrocarbon gases, as natural gas or acetylene gas, in a limited supply of air. It very closely resembles lampblack in most of its properties.

Drop Black (*Vine Black, Ivory Black, Frankfort Black*).—This pigment is made by heating a variety of materials, such as waste cuttings from ivory, vine shoots, cork cuttings, and coconut shell, in retorts or crucibles; the residue contains the greater part of the carbon of the original material. The name "drop black" is applied to this substance because the product after grinding is

mixed with a little glue water and made into pear-shaped drops for sale. Drop black always contains mineral matter resulting from the ash of the burned material, particularly potassium salts, which are somewhat hygroscopic; consequently, it should be washed and dried carefully. It is very black; lampblack appears gray in comparison.

Graphite is an allotropic form of carbon formerly obtained only native as a mineral, but more recently it has been prepared artificially, notably by the Acheson process (page 106). Both the natural and artificial varieties contain impurities, such as silica, iron oxide, and alumina. The natural form contains the greater amount of such substances and, therefore, the less carbon. The natural variety contains about 80 per cent of carbon, while the artificial variety contains about 90 per cent.

Graphite causes very slow drying of the oil with which it is used; the long life of graphite paints may be due to this fact. Not only will the formation of the linoxyn be delayed but the continued oxidation of the linoxyn after it has formed will also be slow. It is this continued or progressive oxidation of the linoxyn of many paint coatings, notably those containing pigments possessed of marked drying properties, that causes the linoxyn soon to become very inelastic and subject to early failure. Since the oxidation is delayed in graphite paints, the film remains elastic for a longer time and, therefore, is much less readily disintegrated.

It seems certain that carbon and graphite are stimulators of corrosion and hence are not to be recommended as constituents of primer coats on iron and steel structures.

Metal Powders.—A number of metal powders have found extensive use in organic coatings to impart color or other desirable properties to the protective or decorative film. Metal powders have the advantage that they require a minimum amount of oil or other vehicle for suitable dispersion and hence yield films that are composed largely of the metal. *Bronze powder* has been used in decorative coatings for many years. More recently, aluminum powder has found wide use in both decorative and protective coatings.[1] Aluminum pigment particles possess a lamellar structure and are covered with an adherent oxide film. In a paint film they appear to arrange themselves horizontally, concentrating in the outer portion of the film and separated from each other

[1] EDWARDS, "Aluminum Paint and Powder," 2d ed., Reinhold Publishing Corporation, New York (1936).

by a very adherent thin film of the vehicle. As a consequence of these structural features, films of aluminum paint are unusually impermeable to moisture, possess good ability to exclude ultraviolet light, and possess unusually high electrical resistance.

Zinc dust or mixtures of zinc dust and zinc oxide are coming into extensive use as pigments in protective coatings for galvanized structures as well as on iron and steel. Zinc dust gives films the well-known battleship-gray color; it seems to impart definite inhibitive properties when present in priming coats on iron and steel. Powders of lead and lead alloys (*e.g.*, Pb, 85 per cent; Sb, 13 per cent; Sn, 2 per cent) also have shown good performance in coatings exposed to a number of types of corrosive environments.

The Lake Pigments.[1]—The lake pigments are made by precipitating some organic coloring matter, usually a coal-tar dye, upon some suitable mineral base, as barytes. The base here is similar in its action to the cloth in ordinary dyeing; it is merely a carrier of the color. In addition to barytes, many other white pigments are used as bases. The colors used should be insoluble in water, oil, and the ordinary solvents used in paints and varnishes. It often happens, however, that they are not thus insoluble and then the coloring matter of the pigment dissolves in the vehicle; in repainting, it may even diffuse through the superimposed layer of paint. If the top coat is of a different color, the diffusion is very objectionable. This diffusion of color is known among painters as "bleeding." It may be overcome by taking advantage of the well-known property of carbon in absorbing coloring matters. Charcoal, lampblack, boneblack, and similar substances possess this property to such a degree that they are used to clarify colored solutions. In repainting over a paint containing a lake pigment, any tendency toward "bleeding" may be overcome by applying first a coat of black paint containing pigments of this sort.

Lake pigments are made up in all colors and are much used in painting. They are usually fairly permanent in respect to light and atmosphere and produce very beautiful effects.

[1] The term "lake" has its origin in the Italian word "lacca," which was the term used to designate the scum that gathered on the top of the vats when dyeing with lac dye, which was much used by the old Italian dyers. Tin and aluminum oxides were used to fix the color on the cloth; the scum consisted of these oxides colored. Since the present lake pigments consist of minerals colored by means of dyes, the English modification of the Italian name has been applied to them.

Some Properties of Pigments.—Some of the more important properties of inorganic pigment substances, such as percentage of 3655-Å. wave length ultraviolet light transmitted by a 0.00092-mm. layer, specific gravity, gallons bulked by 1 lb. of pigment, and oil absorption (pounds of oil needed to form a paste with 100 lb. of pigment) are given in Table 89.

TABLE 89.—PROPERTIES OF PIGMENTS

Pigment	Transmission 3655 Å. light by 0.00092-mm. layer, %	Specific gravity	Bulking value (approx.)	Oil absorption (approx.)
Basic lead carbonate	61	6.4–6.8	0.017–0.019	8–17
Lithopone (30% ZnS, 70% $BaSO_4$)	43	4.3	0.028	11–18
Titanium dioxide	18	3.9	0.031	10–25
Zinc oxide	0	5.57–5.66	0.021	12–21
Zinc sulfide	22	4.0	0.03	10–18
Asbestine	90	2.85	0.042	15–30
Barytes	65	4.46	0.0265	6–12
Silica	85	2.65	0.0453	20–50
Carbon black	0	1.79	0.064–0.069	40–350
Ultramarine blue	85	2.33–2.39	0.05–0.052	28–38
98% chromium oxide	0	5.09	0.0236	11–70
98% lead chromate	4.5	6.00–6.05	0.019–0.020	10–20
Zinc chromate	32	3.28–3.53	0.034–0.036	15–27
98% iron oxide, hydrate	0.5	4.0–4.1	0.0295	20–70

DRYING OILS AND DRIERS

Excluding the mineral (petroleum) oils, which are mixtures of hydrocarbons, and a few other substances to which the name *oil* is applied, the oils in general are esters of high-molecular-weight fatty acids with the polyhydric alcohols such as glycerin. These fatty oils, which are almost invariably of animal or vegetable origin, may be classified for convenience into (1) nondrying, (2) semidrying, and (3) drying oils. Considerable quantities of semidrying and large quantities of drying oils are used annually as the vehicle in protective organic coatings. Roughly, fatty oils of these three classes may be distinguished on a basis of the characteristics of the film formed when a thin layer of the oil is spread on a smooth

surface and exposed to air and light for a few hours. The drying oils assume a comparatively firm, hard surface which does not stick to the finger; the semidrying oils form a film which is more or less firm but remains somewhat sticky (tacky); and the nondrying oils never form a firm film, but remain oily and eventually become rancid.

Film Formation by Oils.—The film-forming properties of oils are related to their molecular structures. In the first place, the oil must be an ester of a fatty acid possessing two or more double bonds between carbon atoms[1]; a single double bond in the acid radical of the ester does not confer drying properties. Furthermore, the presence of conjugated double bonds (*i.e.*, the structure —CH═CH—CH_2—CH═CH—) intensifies the drying tendency of an oil. It is for the latter reason that *tung oil* (*China wood oil* or *wood oil*) and *oiticica oil* possess drying tendencies greater than *linseed* and *perilla* oils. Recently, drying oils have been made from nondrying and semidrying oils; the production of *dehydrated castor oil* from *castor oil* is an important example.

As has been mentioned previously (page 545), the formation of a solid film from a drying oil depends upon the absorption of oxygen. The freshly applied film does not begin, however, to take up oxygen at appreciable rates during an initial induction period, the length of which appears to be determined by the amount of natural antioxidants in the oil. The induction period is shortened by the presence of driers (page 569). The oxygen absorbed is believed to form peroxide linkages at the double bonds in the oil; this step being followed by the splitting off of volatile oxidation products such as low-molecular-weight aldehydes and acids, carbon dioxide, and water. The splitting off of these oxidation products creates a situation favorable to the formation of linkages between the residual molecules of oil with consequent gel formation which immobilizes the film. Once gelation has occurred, no further oxygen absorption can be detected. The initial gel structure (isogel) apparently consists of a continuous three-dimensional solid network surrounded by a liquid phase of about the same chemical composition. Following this, the solid phase gradually grows at the expense of the liquid phase as the gel ages to produce finally a film in which the three-dimensional linkages are quite complete. In this process the film distensibility decreases gradually and, with

[1] McCutcheon, Seltz, and Warner, "General Chemistry," 3d ed., pp. 549, 565, 569, 571, 572, 597, D. Van Nostrand Company, Inc., New York (1939).

sufficient aging, the film becomes brittle. It is generally believed that a solidified film of drying oil has a structure similar to that of resin films.

Drying and Semidrying Oils.—*Linseed oil* is the most widely used of the drying oils. Others, in approximate order of importance, are *tung oil* (*China wood*), *perilla oil*, *oiticica oil*, and *dehydrated castor oil*. The most important semidrying oils from the standpoint of the protective coating industry are *soybean oil* and the various fish oils. Ordinarily, the semidrying oils are not used alone, but are blended with drying oils in proper amount to give the desired film-forming properties.

Linseed Oil.—For the manufacture of paints and varnishes linseed oil is most important. It is obtained from the seed of the common flax, which is grown quite generally over the central, western, and northern portions of the United States, although the bulk of the seed comes from Minnesota and the Dakotas. The flax is cultivated extensively also in Canada, Argentina, India, and southern and western Russia. The seed is usually the sole object of the cultivation; the fiber of the plant is generally wasted.

Linseed oil may be obtained from the seed by any one of three different methods: the hydraulic-press method, the continuous-expeller method, and the extraction method.

The *hydraulic-press method* is the oldest of the three, and much of the oil is still obtained in this way. The seed is crushed to a very fine meal between chilled-iron rolls, and the meal is then heated to about 80°C. with constant stirring. When sufficiently hot, it is molded into cakes weighing about 20 lb. The cakes are wrapped in cloth and pressed with hydraulic pressure, which amounts at a maximum to about 2 tons per sq. in. The seed is pressed but once and the resultant cake, which still contains from 4 to 8 per cent of oil, is used as cattle food. Oil obtained in this way is known as *hot-pressed oil.*

In order to remove suspended particles of meal, the oil is filtered, but this purification is not sufficient since there are always present in a dissolved state certain amounts of albuminous or mucilaginous substances and water. To precipitate dissolved matter as far as possible, the oil is conducted into storage tanks and allowed to stand from 4 to 6 months. The resultant sediment is known as "foots." The longer it is stored the better, since it seems to be characteristic of linseed oil to deposit foots almost indefinitely. The supernatant clear oil is the raw oil of commerce.

Cold-pressed oil is of superior quality but the quantity produced is relatively small. The oil is lighter in color, and more fluid than the hot pressed; it contains less sedimentary matter, probably because it contains less solid fats and foreign substances. About 15 per cent of oil is left in the cake; in consequence, this method is less in favor among the oil producers. In the *continuous-expeller method* the crushed seed is forced by a screw through a cone-shaped grating. The oil trickles through the grating and the pressed meal comes out at the end. This process requires less hand labor than the older method, but allows somewhat more of the oil to remain in the meal.

In the *extraction process* the oil is dissolved from the meal by leaching with petroleum naphtha. The naphtha is distilled from the extract and used over again. It is very difficult to remove the last traces of naphtha, and the oil obtained by this method generally has the odor of the solvent.

The *adulterants* to be looked for in linseed oil are mineral, rosin, corn, cottonseed, menhaden, hemp, and rapeseed oils. The cheapest and perhaps the most frequently used are mineral and rosin oils. If the saponification value (page 568) of linseed oil is low, it may be adulterated with a hydrocarbon oil, as mineral or rosin oil, but a normal saponification value is no proof that the oil is not adulterated. An oil rich in olein, such as cottonseed, might be present; the mixture would still be completely saponifiable. If the iodine value is low (page 568), the adulterant might be either a hydrocarbon oil or an oil rich in olein. If both the saponification and iodine values are low, then a hydrocarbon oil is indicated.

"Boiled" Oil.[1]—The drying of linseed oil may be hastened by the so-called "boiling" of the raw oil. This boiling consists of heating the oil with driers (page 569), sometimes in an open kettle with direct fire or, more usually, in a steam-jacketed kettle or with steam coils, to about 150°C. During the heating, the driers dissolve to some extent and a certain amount of polymerization[2] of the oil is believed to take place. The driers used consist usually of the linoleates, resinates or borates of lead, manganese, and other

[1] It must be understood that the term "boiled" as applied to any of these prepared oils is incorrect, since none of the fatty oils can, in the true sense, be boiled.

[2] A substance is said to polymerize when it changes into another form having the same elements in the same proportion but a higher molecular weight such as would result from a combination of two or more molecules.

metals. Boiled oils prepared with lead driers contract upon oxidizing; those with manganese expand. Usually the two compounds are used together in quantities sufficient to introduce about 0.5 per cent of metallic lead and 0.02 per cent of metallic manganese. Raw oil dries in 3 or 4 days when exposed in a thin layer; the boiled oil dries to a hard film in less than 24 hr., even in as little as 8 hr. indoors, if conditions of temperature and humidity are favorable. This increased rate seems to be due to the fact that the metallic compounds act as catalytic agents. Boiled oil is usually a dark-red color; the color depends upon the amount and kind of drier used, and the length of time and the degree to which the oil has been heated. Boiled oil costs usually about 1 ct. per gallon more than the raw oil.

A "cold-boiled" or "bung-hole" boiled oil is prepared by mixing with the cold or only slightly heated raw oil comparatively small quantities of concentrated solutions of the metallic compounds or driers. These concentrated solutions consist of metallic resinates dissolved in hot linseed oil and turpentine. Such "boiled" oils are quite inferior products.

Bleached Oil.—The glycerides that compose the fatty oils are colorless, but the oils themselves are usually colored to some degree by the presence of impurities. The yellow color of linseed oil is objectionable for the making of white paints and pale varnishes. The color can be removed in a large measure by the oxidation, or some other chemical transformation, of the colored substance. The process generally employed consists of the addition of sulfuric acid and the blowing of air into the oil at the same time. A cloudiness develops after which the oil is allowed to stand until settling takes place, or it is filtered. Various other bleaching agents such as oxides and peroxides are employed. Chemically bleached oil is said to wear not so well as the raw oil.

China Wood or Tung Oil.—This oil is obtained by pressure from the nut of the tung tree, native to China and Japan. The color of the oil varies from pale yellow to dark brown and it has a strong characteristic odor, which may be used as a ready means of identification. During recent years the tung tree has been grown on a considerable scale in the southern part of this country.

Tung oil differs from all the other oils in respect to two rather noteworthy characteristics. In bulk, when exposed to light, a flocculent white precipitate is produced, which gradually increases in amount until after some months the oil becomes a solid whitish

mass. This change is known as the *light break*. When heated to about 250°C. the oil *coagulates* with the formation of a jellylike mass. After cooling it is not again made fluid by heating or by the addition of the ordinary solvents. This gelatinization is believed to be due to polymerization. It is not due to oxygen absorption.

When raw tung oil is brushed out in a thin film, it dries with extreme rapidity, in 30 to 50 min. But raw tung oil is not suitable for paints and varnishes, since its dried film is whitish, opaque, and waxlike, without elasticity. Also, it has a tendency to wrinkle and does not adhere to the surface on which it forms. With proper treatment the oil acquires an ability to dry to a hard, dense, tough, and elastic film, said to be more durable than the linseed-oil film and more impervious to water. The necessary treatment, according to Toch, consists of heating the oil to about 180°C. and adding from 12 to 15 per cent of organic salts of lead and manganese. These organic salts prevent the coagulation. Tung oil is much used in conjunction with linseed oil. In this case the linseed oil is added just subsequent to the organic salt. After sufficient cooling, the prepared oil is thinned with turpentine or benzine or a mixture of both. The treated oil dries much more slowly than the raw oil.

A tung-oil film is less spongy and porous than a linseed-oil film, with consequently less tendency to absorb and allow the passage of moisture. On this account it has proved very useful for the manufacture of enamels, waterproof paints, and varnishes. It is excellent for out-of-door work. Toch says that by the use of tung oil, paints can be prepared that dry well in damp atmospheres. The film from the prepared oil is hard and not readily scratched. When it is used in large amount with a small amount of resin, floor varnishes can be produced that do not show heel marks.

It is claimed that excellent varnishes can be made by the use of tung oil and common rosin or colophony. This is rather remarkable, since rosin lacks hardness and is very brittle. Equally good results are not secured when rosin is used in this way with other oils. The value of the oil has been said to lie in its ability to form actual combinations with the abietic acid of the rosin.

Perilla oil has not been used to any great extent as a paint oil, its use being confined almost entirely to varnish making. It comprises about 36 per cent by weight of the nuts of the plant *Perilla acymoides*, growing in the East Indies, China, and Japan. During the last twenty years this plant has been cultivated to a certain

extent in the United States. It does not have so good drying quality as linseed oil, but it may be greatly improved in this respect by the aid of driers (page 569). One great objection to perilla oil has been its high surface tension which causes creeping and the formation of droplets on the surface of the film. This defect may be offset by blending with oils of lower surface tension or by heat-treating and blowing at about 260°C. (500°F.) to increase the viscosity. Exposure tests on perilla oil films show them to be as durable as ones made from linseed. Driers dissolve readily in this oil; when lead or manganese compounds are used as driers, the oil should be blended with about 30 per cent of linseed. Cobalt driers may be used without the addition of linseed to yield an extremely glossy film.

Oiticica oil is obtained from the *Licania rigida* which grows chiefly in Brazil, and is mostly heat-treated to give a permanent drying oil. It has a characteristic greenish color due to chlorophyll. Half a million pounds of this oil were imported in 1940, and its use is increasing rapidly. It forms films that are more brittle and less resistant to water, alkali, and heat than films of tung oil. It has been found, however, that this oil may to a certain extent be substituted for tung oil in tung-linseed varnishes in which the tung oil content is not too high. A glyceride of licanic acid, a γ-keto acid containing three conjugate double bonds in an 18 carbon atom chain, is considered to be the drying constituent of this oil.

Dehydrated castor oil, originally made by the destructive distillation of castor oil, is now made almost entirely by catalytic dehydration and vacuum distillation. Like oiticica oil, this is one of the comparatively new products that are under investigation as substitutes for tung oil. It seems to be more favorably regarded than oiticica oil by the varnish manufacturers. "Synthenol," "Isolene," "Dehydrol," and "Castung" are trade names for this product made by various manufacturers. Approximately 5 million pounds of dehydrated castor oil were made in 1940, and developments seem to point toward a continued increase in its use.

When used in varnish manufacture, it is necessary to body the oil by heat-treatment to a 2 to 3 viscosity (bubble test) to make it similar to tung oil. It has a longer gelation time than tung oil, which is a desirable feature in handling a batch in the varnish kettle.

Soybean Oil.—The soybean is native to Manchuria, but has been rather extensively introduced into the United States, especially

in the southern portion. There are as many as 280 known varieties, and more may exist. All varieties do not yield oil suitable for paints; much of it is used for making food products and soaps.

From 10 to 15 per cent of oil is obtained from the soybean by the method of hot pressure. Except that it has perhaps a slightly darker color, it is very similar in all its physical characteristics to linseed oil, so that it is somewhat difficult to distinguish between the two. Soybean oil contains about 15 per cent of saturated fats, largely palmitin. The unsaturated fats are chiefly the glycerides of oleic and linoleic acids, about 56 per cent of the former and 20 per cent of the latter.

The raw oil produces an elastic film but dries rather slowly, although it can be converted into a very suitable drying oil by the use of the proper driers, which according to Toch, are mixtures of the tungates and resinates of lead and manganese. The tungates are the soaps produced by the reaction of lead and manganese compounds with tung oil. The resinates are the products of the reaction of the metallic compounds with common rosin. The soybean oil is said to dry to a hard resistant film in 24 hr. when used with 5 to 7 per cent of this drier. It is very susceptible to the drying action of the tungate of trivalent cobalt, but the cobaltous compound is not active. The film of soybean oil is said to wear not so well as that of linseed oil for exterior use, but is reported to be equally good for interior work. The oil is not used alone but in conjunction with linseed oil.

Fish oils, of which *menhaden* oil is the most important, have been used for many years as semidrying oils. They generally are used in conjunction with drying oils such as linseed. In smaller amounts, oils from sardines and other fish are used in the industry. Recently, research has been directed toward obtaining a drying oil from whales. Improvements in collecting and refining these oils have overcome to a great extent their objectionable odor and have made them more satisfactory as substitutes for more expensive drying oils. They are not suitable for paints in the raw state but, when treated with tungate and resinate driers, they become fair drying oils. They do not blister and peel so readily as other paint oils when exposed to elevated temperatures and the weather. For this reason they are especially suitable in coatings for smokestacks and boiler fronts. Films of dried fish oil have good water resistance.

Rosin Oil.—Although this oil is not a fatty oil and does not possess to any extent the properties that a good paint oil should

have, it is nevertheless frequently introduced into paint oils as an adulterant. On this account, mention is made of it here.

When rosin is subjected to destructive distillation, various decomposition products are obtained. Chief among these products is rosin oil; there is about 85 per cent of it in the distillate. The crude oil is dark and viscous, with a marked characteristic odor and, because rosin is carried over mechanically to a small extent during distillation, it is acid in character. The oil is refined and various grades are produced with colors varying from dark red to pale yellow. The refined oil consists almost entirely of hydrocarbons and is unsaponifiable. It has a bluish bloom or fluorescence, which is less pronounced in the more highly refined oils. It dissolves readily in ether, chloroform, turpentine, and petroleum spirit. It has some drying properties due to oxygen absorption. It is among the cheapest of all the oils and is consequently much used to adulterate other oils.

TABLE 90.—PROPERTIES OF DRYING AND SEMIDRYING OILS*

Oil	Specific gravity 15°/15°C.	Refractive index	Saponification value	Iodine value	Acid value
Linseed	0.930–0.938	1.4835(22°C.)	188–195	175–202	1.0–3.5
Tung	0.939–0.949	1.5030(19°C.)	190–197	163–171	2.0
Perilla	0.928–0.937	1.4815(25°C.)	188–194	185–206	1.0–5.0
Oiticica	0.967–0.977	1.5090–1.5141(25°C.)	186–192	....	4.0–6.0
Dehydrated castor	0.954–0.958	....	188–194	112–120	3.5–6.0
Castor	0.960–0.967	1.4773(25°C.)	175–183	84	0.12–0.80
Soybean	0.924–0.927	1.4762(15.5°C.)	189–193.5	122–134	0.3–1.8
Menhaden	0.923–0.933	1.480(15.0°C.)	189–192.9	148–185	3.0–11.6

* The larger treatises on drying oils should be consulted for a discussion of the influence of various refining and other treatments upon the value of these oil characteristics.

Properties of Drying Oils.—The chief properties which determine the suitability of fatty oils for special purposes and which are used for their identification and specification are the following: (1) the *specific gravity*. (2) The *saponification value*, which represents the number of milligrams of potassium hydroxide required for the complete saponification of one gram of the oil. In this test potassium hydroxide is consumed in neutralizing any free acid as well as in saponifying the glyceryl esters present. (3) The *acid value* which is equal to the number of milligrams of potassium hydroxide required to neutralize completely the *free* fatty acid in

one gram of oil. The difference between the saponification number and the acid number is known as (4) the *ester number*. The acid value and the saponification number can be used to detect adulteration by unsaponifiable substances and to determine the mean molecular weight of the fatty acids in the oil. (5) The *iodine value* represents the number of centigrams of iodine taken up by one gram of oil. The absorption is due mainly to direct addition of iodine at the double bonds in the oil molecule, but may in part consist of substitution of iodine for hydrogen atoms. The iodine value thus gives information on the extent of unsaturation in the oil, a structural feature that has previously been related to the oxygen-absorbing and drying qualities of the oil.

For the details of making and interpreting the above and other standard tests on oils, the reader is referred to the larger treatises.[1] Some of the properties of the common drying and semidrying oils are given in Table 90.

Driers.[2]—For many years substances called driers have been added to the drying oils used in the production of organic protective coatings to accelerate the rate of drying of films, and to a certain extent to control the physical properties of the film. They function as catalysts in the addition of oxygen at the double bonds in the oils during the early part of the drying period; their presence appreciably shortens the induction period (page 561) and accelerates the formation of the polar groups necessary for film formation. The tensile strength, elasticity, and other physical properties, as well as the aging properties of the film are influenced by the amount and kind of drier used. Driers, in general, are organic compounds of those metals which are capable of readily existing in several states of oxidation. Most extensively used are the resinates, linoleates, and naphthenates of lead, manganese, and vanadium. Cobalt driers influence especially the surface-drying properties of oils, whereas manganese and lead compounds affect the through drying of the film. It is therefore necessary to maintain a careful balance of various driers in any product, especially when the film is

[1] FURMAN (editor), "Scott's Standard Methods of Chemical Analysis," Vol. II, 5th ed., pp. 1764–1801, 1839–1877, D. Van Nostrand Company, Inc., New York (1939). LEWKOWITSCH, "Chemical Technology and Analysis of Oils, Fats and Waxes," 3 vols., The Macmillan Company, New York (1921–1923). GARDNER, 9th ed., pp. 284–305.

[2] KRUMBHAAR, "Chemistry of Synthetic Surface Coatings," pp. 45–67, Reinhold Publishing Corporation, New York (1937). ELM, *Ind Eng. Chem.*, **26**, 386 (1934). GARDNER, 9th ed., pp. 306–311.

to be exposed to elevated temperatures during drying. Driers are used in relatively small amounts; *e.g.*, 0.50 per cent of lead or 0.05 per cent of manganese when used alone in linseed oil (percentages on a basis of metal content).

Driers may be incorporated in an oil by adding oxides or other inorganic compounds to the oil and heating, the inorganic compounds being converted into organic metallic compounds that are soluble in the oil. However, the favored practice is to prepare an oil-soluble organic compound of the metal separately, and then add a solution of the compound in a thinner such as turpentine or benzine to the oil. The latter practice has the advantage that the drier content of a product can be carefully regulated in a quantitative manner. These solutions of driers are frequently called *japan driers.*

Resins, Cellulose Derivatives, and Plasticizers

On a basis of their performance and behavior, resins may be defined as natural or artificial mixtures of organic substances which are soluble in organic solvents at some stage in their development and, when deposited from suitable solvents, form a continuous adherent film. In general, the resins do not crystallize when deposited from solvents and they possess a softening range rather than a sharp melting point. The resinous state is a consequence of the development of large molecules of varied size and shape. As a consequence, resins are obtained from a great variety of natural and artificial sources and possess great diversity of chemical compositions.

For many years resins of suitable properties have been used either alone (spirit varnishes), mixed with drying oils (oleoresinous varnishes and enamels), or mixed with cellulose derivatives (lacquer enamels) as the vehicle or film-forming part of organic protective coatings. Resins are frequently classified on a basis of source into natural resins and synthetic resins. It must be emphasized, however, that this classification has no basis from the standpoint of their physical behavior.

Natural Resins.—With one important exception, namely shellac, the natural resins originate from the exudations of plants and trees growing in many parts of the world. When accidentally or intentionally wounded, these plants and trees exude water-insoluble resinous materials from their resin ducts as a protection against the wound. When first exuded, these "resins" (balsams) are

relatively fluid and readily soluble in a great variety of solvents, but after exposure, volatile constituents are lost and the residue undergoes oxidation and other complex reactions with a consequent increase in the softening temperature and chemical inertness of the resin, and a decrease in its solubility in the usual solvents. The exudations of the past have accumulated on the ground or become buried. As a consequence, natural resins are available that represent practically all stages in the transition from the freshly exuded *balsams*, through the "recent" resins, the "recent fossil" resins to the "fossil" resins. One of the most important recent resins is *rosin* and the oldest fossil resin is *amber;* in between are the various mastic, sandarac, elemi, dammar, copal, kauri, and other resins.

Rosin or *colophony* is the residue left after turpentine has been distilled from the balsam obtained from certain varieties of pine. In the United States the principal source is from the long-leaf, yellow, or hard pine found chiefly in the Carolinas, Georgia, and Florida. Rosin consists chiefly of abietic acid, but contains other constituents that restrain crystallization. It is graded according to color, the grades being indicated by the letters *A*, *B*, *C* . . . to *N*; *A* being the darkest grade. Two lighter grades are designated as *WG* ("window glass") and *WW* ("water white"). The average molecular size in rosin is small which makes it questionable whether rosin should be classified as a resin. As a matter of fact, rosin without modification finds little use directly as a film-forming constituent of protective coatings. Its chief importance to the paint and varnish industry lies in the fact that it can be hydrogenated, oxidized, esterified, and otherwise converted into film-forming materials of a wide range of physical and chemical characteristics. Chief among these derivatives of rosin is *ester gum*, made by esterification of the rosin acid with glycerin.

The resinous state is more clearly developed in such recent resins as *elemi*, *mastic*, *sandarac*, and *dammar*. These are soluble in a wide variety of solvents and, when blended with the older fossil resins, add toughness to the resin film due to their plasticizing action. Next in order of age come the *copals*, which are available in a great variety of grades on a basis of color, solubility, and hardness, and bridge the gap between the more recent resins listed above and the much older kauri resins. The copals have found extensive use in varnish making. Owing to their restricted solubility, they must be partly depolymerized by heat-treatment

before being blended with hot oils and other resins in the varnish kettle.

Kauri resins are intermediate between the copals and the most ancient *ambers*. The latter are too rare to be used to any great extent; hence the kauri resins are the oldest fossil resins that find extensive use in the paint and varnish industry. Like the copals, their color, hardness, solubility, and other physical and chemical characteristics depend upon their age, which for these resins may run to thousands of years. Owing to their low degree of solubility or "compatibility," they must be depolymerized by heat-treatment or "running" before use in the production of a varnish.

The important natural resin which is not of plant origin is *shellac* (*lac resin*). It is produced by a parasitic insect that feeds on a variety of host trees found principally in India. These tiny insects, of the Coccidae family, suck up the sap of the tree and excrete a substance that dries to form a protective incrustation. The insects are so thickly clustered that the incrustations grow together and form a layer that eventually covers the twig entirely. They come to maturity several times each year, at which times the twigs containing the resinous incrustation are cut or broken off and constitute the product known as *stick lac*. Before marketing, the lac is refined to various degrees. Generally the resin is separated from the twigs by rolling or crushing, then agitated with warm water which extracts much of the coloring matter from the resin. The resin is taken up from the bottom of the vat and dried by exposure to the atmosphere. In this condition it is known as *seed lac*. Formerly, arsenic sulfide was added at this point to produce a uniform golden coloration, but this practice is being curtailed because it serves no useful purpose.

Seed lac usually is graded and then, by further treatment, converted into one of the commercial varieties of lac, such as *shellac*, *button lac*, or *garnet lac*. For the organic coating industry, shellac is the important variety. It is prepared by drying washed seed lac in the sun, carefully heating it inside cloth bags from which it is expressed, and then stretching it by hand into large thin sheets. The flake shellac of commerce is made from these sheets, the grade depending upon the grade of seed lac employed.

Bleached shellac is made by dissolving shellac in alkali and treating with a solution of sodium hypochlorite. After the shellac is bleached by the oxidizing action of the hypochlorite, it is reprecipitated by neutralizing the alkali with sulfuric acid.

Shellac is soluble in both methanol and ethanol, although the latter does not dissolve it properly if more than 5 per cent of water is present in the alcohol. It is only slightly soluble in ether and chloroform and is almost insoluble in turpentine. Owing to its combined hardness and elasticity, shellac is the best of the resins for use in making spirit varnishes. Solutions of shellac in alcohol find wide use as an indoor organic coating material. They dry quickly to form a hard continuous film of low permeability and good adherence. It also is used extensively as an electrical insulator, as a binder in abrasive wheels, and in many forms of composition goods.

Synthetic Resins.—During recent years, no field of chemical research has been more active than that devoted to the development and production of synthetic resins from readily available, cheap raw materials. Although it would be unsafe to say that synthetic resins are now available that possess properties superior to the natural resins, these materials do offer a number of important advantages to the organic coating technologist: (1) They furnish a dependable supply of resins from abundant raw materials such as cellulose, petroleum, coal, limestone, air, salt, and water, which are independent of imports and world markets. (2) Synthetic resins may be "tailor-made" with the physical and chemical characteristics best suited for a given application.

Some idea of the complexity of the field can be gained from the fact that there are several hundred synthetic resins that are of interest to the industry. Many of these are the same substances, or are similar to the "plastics" that are described in Chap. XVII. Only a brief mention of those types which have an established position in the paint, varnish, and lacquer industry will be made here.

Phenol aldehyde type resins when used in varnishes yield a product of excellent durability when exposed to high humidity, water, and a number of chemical reagents that attack the older types of paints and varnishes. Furthermore, these phenolic resins have been improved so that they have satisfactory color stability when exposed to light, a defect that formerly limited their use. Phenol aldehyde resins suitable for molding compositions are not suitable as paint and varnish vehicles because of their low compatibility with drying oils. Resins of suitable compatibility may be produced by (1) replacing ordinary phenol by a phenol that contains a substituent group of at least three carbon atoms in the *para*

position to the hydroxyl group, thus producing the so-called *straight oil-soluble* phenolic resin. (2) The ordinary resin may be modified by fluxing with natural resins, ester gum, or rosin to produce an oil-soluble mixture.

The *glyptal* or *alkyd* resins, made by the esterification of a polyhydric alcohol such as glycerine with a polybasic acid or acid anhydride like phthalic anhydride constitute another extremely important class of synthetic resins for the paint industry. A wide range of physical characteristics may be obtained in these resins by replacing a part of the phthalic anhydride with natural resins, other polybasic acids, drying oils, etc., or by other modifications in the process of manufacture. These resins can be used to produce coatings that are converted to a solid film with or without oxygen, and with or without heat. The heat-converted films, especially, are tough, nonyellowing, chemically stable, and durable.

Almost all the high-molecular-weight polymers, copolymers, and condensation products (page 532) that have been developed in the plastics field have been examined to determine their possibilities as constituents of organic coatings, and many of them have found definite fields of usefulness.

Among the other synthetic resins that have been developed for use in coatings, mention should be made of the paracoumarone and paraindene resins ("Cumar") made by polymerizing coumarone and indene obtained from coal-tar light oils; the resins obtained by polymerizing olefins produced in petroleum refining; and the chemically inert resins obtained by polymerizing rubber by treatment with chlorine ("chlorinated" rubber).

Cellulose Derivatives.—Native cellulose (*e.g.*, cotton) must be considerably degraded (depolymerized) and converted to such derivatives as esters and ethers before the desired film-forming characteristics are attained. Cellulose degradation and conversion also are necessary to obtain sufficient solubility or dispersing tendency in available solvents, and to obtain solutions of sufficiently low viscosity that they may be brushed or sprayed on a surface and yet deposit a film of suitable thickness. The most important cellulose derivatives are the esters, cellulose nitrate, cellulose acetate, and cellulose acetobutyrate, and the ethers, methyl and ethyl cellulose. These substances have most of the film-forming characteristics of the resins except that their films lack adherence and have a pronounced tendency to wrinkle. For these reasons, suitable resins are incorporated in lacquers to provide film adher-

ence, and plasticizers are added to improve the flow of the lacquer just before it sets and to improve the toughness, elasticity, and smoothness of the film.

Plasticizers.—These substances whose function has been mentioned above are liquids or low-melting-point solids of extremely low volatility. They therefore remain a permanent part of the dry film. When cellulose nitrates were first employed in lacquers, the raw material was celluloid and the camphor in the celluloid acted as a plasticizer for the cellulose nitrate film. Camphor, however, is not an especially suitable plasticizer because it has a sufficiently high vapor pressure to sublime slowly from the film with the result that the film ages rapidly, becomes brittle, and soon disintegrates. For this reason, camphor was replaced by castor oil which is practically nonvolatile. Owing to its tendency to oxidize and become rancid on exposure, castor oil has now been largely replaced by other more satisfactory plasticizers. Of the hundreds of plasticizers available today,[1] tricresyl phosphate, triphenyl phosphate, dibutyl phthalate, dibutyl tartrate, and diamyl phthalate may be mentioned as typical.

SOLVENTS AND DILUENTS

To apply organic coatings to surfaces by brushing, spraying, or dipping at ordinary temperatures, it is necessary to dissolve or disperse the film-forming ingredients and pigments in suitable organic liquids which act as solvents, diluents, or thinners. In addition to their function in providing easy application, thinners must be selected so that the film-forming ingredients will be deposited as an adherent, smooth, and fairly nonporous film as the thinner evaporates. Obviously, the volatility of the thinner is comparable to its solvent power in importance. Thinners that actually dissolve film-forming substances such as drying oils, resins, and cellulose derivatives may in the strict sense be called solvents. Those which would not by themselves dissolve the film-forming constituents should be called *diluents*. It is frequently possible, however, to add cheaper diluents to solvents of good solvent power and thereby improve the volatility characteristics of the thinner as a whole and also reduce its cost.

The most important paint and varnish thinners are petroleum (mineral) spirits or naphthas, turpentines, and hydrocarbons from coal tar. Methanol and ethanol are the important solvents for

[1] GARDNER, 9th ed., p. 575.

shellac. For use in lacquers and lacquer enamels a great variety of solvents are available, many of which are commercially pure chemical compounds. The chief diluents in lacquers and lacquer enamels are the petroleum and coat-tar hydrocarbons.

In general, a mixture of liquids of different volatilities makes a more satisfactory thinner than a pure compound. If the volatility of the thinner is too high, the cooling effect due to rapid evaporation will cause condensation of moisture on the film, a defect known as "blushing." On the other hand, if the volatility of the thinner is too low, the film remains tacky too long. The volatility of a thinner can usually be estimated from a distillation test in which the boiling range is determined.

Turpentines.—These widely used solvents are produced from the balsam exuded from pine trees, already mentioned as the source of rosin, or from the resinous material in the wood of dead pines and pine stumps. That obtained from the former source is called *gum spirits* of turpentine and that from the latter source is known as *wood* turpentine.

In the production of gum spirits turpentine, the balsam is placed in copper stills and distilled, usually with steam. Without steam the heating must be very carefully controlled or inferior grades both of turpentine and rosin will be produced. After condensation, the turpentine and water separate into layers. The balsam yields from 10 to 25 per cent of turpentine.

Turpentine is a water-white, volatile liquid consisting chiefly of pinene, $C_{10}H_{16}$. It is used in paints and varnishes to dilute them and to increase their flowing qualities. It is exceptionally suitable for this purpose, because, although it is volatile, it does not evaporate rapidly; hence, it keeps the freshly applied film fluid for a sufficient length of time that the marks of the brush, which are unavoidable, will flow out and disappear. Many of the turpentine substitutes, for example some of the light petroleum products, *i.e.*, gasolines and naphthas, are too highly volatile; they allow the film to lose its fluidity before the irregularities have been eliminated. Petroleum products can be prepared, however, that very closely resemble turpentine in this important property.

Turpentine has a characteristic aromatic odor, which, in small quantity is not unpleasant; but if breathed for an extended period, it may become objectionable. Upon some persons it has a marked physiological action, causing headache and nausea; upon others it produces no ill effects.

With continued exposure to the air, turpentine undergoes oxidation with the formation of an aldehyde $C_{10}H_{16}O_3$. The sharp odor of old turpentine is due to this. By continued oxidation it turns yellow, thickens, and forms a semisolid, sticky, resinous mass. By this reaction with oxygen, small amounts of ozone and hydrogen peroxide are produced.[1] Turpentine that has thus thickened is no longer desirable as a paint and varnish solvent or diluent. All turpentines are not equally susceptible to oxidation; some remain clear and thinly fluid for a long time, and others thicken within a few weeks. The change is more likely to occur when the turpentine is kept in containers that are only partly filled, or when they are loosely stoppered or opened frequently.

The fact that turpentine reacts with oxygen in the manner described, producing by-products possessed of a distinct oxidizing character, is claimed by some to be a matter of importance in connection with the drying of paint and varnish oils. To whatever degree the turpentine functions in this manner, it is an ideal drier. Not only is the drying of the oil promoted during the critical period when it is most desired, but by the time the film has dried, the drier will have ceased to act. With the usual driers, the oxidizing effect continues even after the film has acquired solidity, with the result that the elasticity of the film is destroyed and its failure is hastened.

Because it is an excellent solvent for all fatty oils and evaporates at the desired rate, turpentine is eminently suitable as a diluent or thinner for paints and the oil varnishes, but it is not a solvent for linoxyn and other dried oil films, nor is it a solvent for pyroxylin, *i.e.*, the cellulose nitrate or acetate lacquers. Turpentine dissolves also the mineral oils. The mineral waxes, such as paraffin wax and ozocerite, dissolve in turpentine to a moderate degree, but beeswax is readily soluble. A solution of the latter in turpentine is extensively used as a furniture polish. Turpentine dissolves the soft resins such as rosin, dammar, and Manila copal, but it does not dissolve the hard copals (page 571) until after they have been fused and incorporated in oil. Shellac resin is insoluble in turpentine.

Although water dissolves in turpentine to a slight degree, turpentine is practically insoluble in water. Turpentine is miscible in all proportions with gasoline and kerosene, with benzol, with propyl, butyl, and amyl alcohols, amyl acetate, and acetone, but

[1] Note the bleaching of the cork stopper of a bottle in which the turpentine has stood for some time.

with absolute ethyl alcohol its miscibility is only partial; with absolute methyl alcohol it is practically immiscible.

Iron vessels are unsuitable containers for turpentine. It causes the metal to corrode, particularly at the surface of the liquid. Zinc-coated ware is also affected by it. In contact with iron, the turpentine acquires a reddish, and in contact with zinc, a whitish turbidity, produced by its reaction products with the metals. Turpentine is generally stored in tinned iron or wooden containers. Turpentine is expensive. It is consequently liable to adulteration with mineral-oil products, usually benzine and kerosene, which cost considerably less than half as much.

Wood turpentine is obtained by distillation of the wood, such as stumps, knots, and old trunks of turpentine-producing trees. Its composition differs somewhat from the "gum spirits," containing a noteworthy amount of dipentene in addition to the pinene, but as far as its physical effects in paints and varnishes are concerned it is as suitable as the turpentine obtained from the balsam. It contains 2 or 3 per cent of impurities, however, such as pyroligneous and formic acids, creosote, and pyridine bases; and unless the turpentine has been carefully refined, it has a disagreeable odor that makes it somewhat undesirable for interior use. In recent years, a *steam-distilled* wood turpentine has been widely used. This product is free from objectionable impurities and has an odor that is nearly as pleasant as gum spirits turpentine.

Petroleum Hydrocarbons (*Petroleum Spirit, Turpentine Substitute*).—In the refining of petroleum oils, the light distillate first obtained is refractionated into several grades according to the volatility required by the use for which the fractions are intended. The methods of refining and the grades commonly produced are described on pages 82 to 84.

Petroleum spirit designed for use as a paint and varnish thinner must have a carefully regulated volatility. Although it must be completely volatile at ordinary atmospheric temperatures, it must not be too volatile, or the paint film will set before it has acquired a smooth surface. In the distillation test, the initial boiling point should not be lower than 150°C., and the end point should not be higher than 210°C. Ninety per cent should distill below 200°C. If too great a quantity of hydrocarbons that are difficultly volatile, such as those of the kerosene type, are present, the paint or varnish in which the thinner is used will remain indefinitely soft and sticky. The escape of even a readily volatile thinner is difficult after a film

has begun to solidify. With turpentine, the presence of a small residue of low volatility is less objectionable, because polymerization and oxidation will convert any unevaporated portion of that solvent into a solid mass that will be compatible with the remainder of the film. The petroleum hydrocarbons do not respond in this manner.

Another comparison that may be drawn between turpentine and the petroleum solvent is, that because of its chemical inertness the latter does not serve as an oxygen carrier, to promote in the manner of turpentine the oxidation of the drying oils. On the other hand, the petroleum spirit is greatly preferable to turpentine with respect to its odor.

Petroleum spirit is immiscible with water, but, with the exception of methyl and ethyl alcohols, it mixes in all proportions with most of the other organic solvents. Even the methyl and ethyl alcohols become soluble in petroleum spirit in the presence of a higher alcohol, such as butyl or amyl.

With the exception of castor oil, all fatty, mineral, and rosin oils are soluble in petroleum spirit, but it is not a solvent for the oxidized oils such as linoxyn. It easily dissolves freshly prepared rosin, but old rosin is only partly soluble. Other soft resins are partly soluble in the petroleum spirit, but the hard resins are practically insoluble. The petroleum hydrocarbons are not solvents for cellulose nitrate.

Coal-tar Distillates.—One of the products resulting from the destructive distillation of coal consists of light tar oils. Among the many compounds that appear in the condensate when these oils are fractionated are benzene, C_6H_6, toluene, $C_6H_5{\cdot}CH_3$, and xylene, $C_6H_4{\cdot}(CH_3)_2$. They are all water-white, limpid liquids, with not unpleasant, aromatic odors. Benzene boils at 80.5, toluene at 111, and xylene at 139°C.

The ordinary commercial benzene consists of about 70 per cent of benzene and 25 per cent of toluene, with small amounts of other compounds. It is a good solvent for oils, fats, and soft resins, but it is not a solvent for cellulose nitrate. It is miscible in all proportions with the other organic solvents, but it does not mix with water.

Solvent naphtha is a mixture of these coal-tar aromatic hydrocarbons.

Other Solvents.—A large number of organic liquids are used, either alone or mixed with one or more liquids, as solvents and

thinners, especially in lacquers and lacquer enamels. Gardner in the 9th edition of his treatise on "Paints, Varnishes, Lacquers and Colors" lists about 150 organic compounds that are of interest to the lacquer technologist as solvents. Most of these compounds are alcohols, ketones, esters, ethers, and compounds that may have the characteristics of alcohols and ethers in the same molecule (*e.g.*, cellosolve). Only a few of the more important of these compounds are listed in Table 91.

TABLE 91.—PROPERTIES OF SOME ORGANIC SOLVENTS

Solvent	Boiling range, °C.	Solvent characteristics*
Methyl alcohol (methanol)	63–67	Dil. for N.C. and C.A. Sol. for some resins
Ethyl alcohol (ethanol)	77–80	Dil. cosol. for N.C. Sol for some resins
n-Butyl alcohol, C_4H_9OH	115–118	Dil. cosol. for N.C. Dil for C.A. Sol. for resins
n-Amylalcohol, $C_5H_{11}OH$	136–140	Dil. cosol. for N.C. Sol. for oils and soft resins
Dimethyl ketone (acetone)	55–57	Sol. for N.C., C.A., and resins
Methyl ethyl ketone, $CH_3COC_2H_5$	70–82	Sol. for N.C., C.A., and resins
Ethyl acetate, $CH_3COOC_2H_5$	73–80	Sol. for N.C. and C.A.
Butyl acetate, $CH_3COOC_4H_9$	120–125	Sol. for N.C. and C.A.
Amyl acetate, $CH_3COOC_5H_{11}$	110–150	Sol. for N.C.
Ethyl lactate, $CH_3CHOHCOOC_2H_5$	120–170	Sol. for N.C. and C.A.
Diethyl ether, $C_2H_5OC_2H_5$	34–37	Cosol. for N.C. Sol. for fats, oil, and resins
Dioxane, $C_4H_8O_2$	101	Sol. for N.C., C.A., and some resins
Cellosolve, $CH_2OHCH_2OC_2H_5$	132–137	Sol. for N.C.
Cellosolve acetate	145–165	Sol. for N.C., C.A., and resins

* Dil. = diluent; N.C. = nitrocellulose; C.A. = cellulose acetate; sol. = solvent; cosol. = solvent.

The entire thinner for a lacquer or lacquer enamel is likely to be a mixture of at least three types of substances such as an alcohol, an ester, and a hydrocarbon diluent. These are properly selected and proportioned to give suitable solubility for the resin and the cellulose derivative, and the proper rate of evaporation after application.

Paint and Varnish Removers.—There are a number of liquids that exert a solvent action on dried paint and varnish films, but

being highly volatile also, they do not remain in place long enough to become effective. Consequently, if the liquids are entangled in some medium that will serve to prevent their evaporation and the whole is applied in a paste form, they may be advantageously used. A reference standard used in writing specifications on these organic solvent-type removers is made by dissolving 3 parts by weight of paraffin wax (m. p. about 55°C.) in 50 parts of benzene, C_6H_6, and adding to this a solution of 25 parts of acetone in 25 parts of 95 per cent alcohol.

A number of the solvents employed in the lacquer industry, which have already been described, are also finding application as paint and varnish removers. Among those that are used for this purpose are methyl ketone, methyl ethyl ketone, and butyl alcohol.

An active preparation of an entirely different sort is the following, used also in paste form: caustic soda, 1 part; fresh powdered quicklime, 3 parts; and whiting 4 parts, with sufficient water to form a paste. This is applied and allowed to remain for a short time. This preparation is active because it converts the linoxyn into soap. Or a 10 to 12 per cent solution of sodium carbonate may be used, as may also a moderately concentrated solution of ammonium hydroxide. These liquids are used with an abrasive as steel wool, or a stiff-bristled brush. After the removal of paint or varnish by any one of these alkaline substances, the residual alkali on the surface of the wood must be corrected with some weak acid, as for example, about a 5 per cent solution of oxalic acid, which both neutralizes the alkali and acts as a bleaching agent.

Special Coatings and Related Materials

There are numerous protective organic coatings that do not fall in the principal classes discussed in the early part of this chapter. The more important of these will be briefly described in this section.

Bituminous Coatings.—Of these coatings, the air-blown asphalts from asphaltic base crude oils (page 79) and the coal tars have found the greatest use. They may be applied hot without a thinner, at ordinary temperatures with a thinner, or in the form of asphalt-water or tar-water emulsions. In certain circumstances, these relatively cheap coatings may give protection at lower over-all cost per year than any other known coating; *e.g.*, bituminous coatings are widely used for the protection of pipe lines and iron and steel structures that are in contact with or buried in soil. A typical pipe-line coating is represented by the following: the clean

pipe is first given a cold primer coat of bitumen dissolved in a thinner. After the primer coat has dried, a thick hot coating of blown asphalt or coal-tar enamel is applied. The hot enamel coat is immediately wrapped spirally with burlap or preferably with an impregnated asbestos fabric. For a high-grade coating a second hot enamel coat is then applied followed by another wrapping with asbestos felt and a final wrapping of kraft paper. Special machines have been designed to apply these coatings either in the field or in the factory. Bituminous coatings such as the one described above will range from $\frac{1}{32}$ to $\frac{1}{2}$ in. in thickness. By applying a coating of specified thickness in several layers instead of one, the final coating will be less likely to possess imperfections such as pinholes. For some applications, mineral fillers and "plasticizers" are added to the bitumen. Most authorities claim that coal-tar coatings are less permeable to moisture than are those of blown asphalt.

Bituminous coatings also are frequently applied to concrete structures to lower their moisture permeability. It is claimed that the bitumen-water emulsions may be applied successfully to wet concrete.

Nondrying Protective Coatings.—There are a great variety of these products on the market; most of them bear trade names. They have amorphous waxes (page 95) or greases (page 104) as their chief constituents; some contain in addition organic-type corrosion inhibitors, others contain chromates as inhibitors, and still others have zinc dust as a constituent. Most of them are stiff enough so that they will not flow from a metal surface at temperatures below 100 to 150°F. There seems little doubt that many of these materials will give temporary protection to iron and steel structures, the duration of the protection depending upon the conditions of exposure. In aqueous environments, protection can be expected for only short periods because liquid water seems gradually to displace practically all coatings of this type.

Wax Polishes.—The paste polishing and finishing waxes usually are gels of wax in petroleum naphthas or in mixtures of naphthas and turpentine. The wax base usually contains an appreciable percentage of a hard wax such as *carnauba* wax. The "liquid" waxes are either suspensions of wax in the same type of solvent used in the paste waxes, or are suspensions of wax in water stabilized by the addition of soaps. The "no-rub" polishing waxes are of the latter variety. The good grades of polishing and finishing

waxes furnish excellent protective coatings for interior woodwork, furniture, hardwood floors, and linoleums.

Cold-water Paints.—For each essential ingredient of an oil paint a water paint contains a component with a similar function. As has been mentioned, an oil paint consists of finely ground mineral matter suspended in an oily medium containing an insolubilizer, called a drier, and an organic solvent, or thinner, to lessen the viscosity. Water paints contain finely ground mineral pigments with a binder and an insolubilizer; water is the solvent and thinner. In oil paints, the dried oil becomes the binder. The binders employed in water paints are generally casein, soybean protein, glue (page 591), dextrine, and silicate of soda, the first three of which are the most important. For casein, which makes the best water paint, the insolubilizer is calcium hydroxide. Glue may be rendered at least partly insoluble by alum, or by a dichromate in the presence of light.

Casein Paints.—If a suitable mixture of finely ground casein (page 602) and powdered slaked lime is worked into a paste with water, the calcium hydroxide coagulates the casein and causes it to become insoluble when dried. Use is made of this fact in preparing washable cold-water paints in which casein acts as a binder to hold the pigment particles together. Casein paints are comparatively cheap, are easy to apply, and may be used on practically any type of surface. Because they are not injured by free lime, they may be used on stucco, where oil paints cannot be used advantageously (page 588).

Distempers and Calcimines.—Preparations of this kind are usually mixtures of pigments with glue dissolved in water. In distempers a small amount of alum may be used to act as an insolubilizer for the glue, but the product is only damp resisting and is not weatherproof. If the surface to which distemper is applied is exposed to bright sunlight, the addition of sodium bichromate in an amount equal to about 3 per cent of the weight of the glue will render the glue practically insoluble, but even this preparation is not weatherproof.

Calcimines are similar to distempers, but no insolubilizer is used; they are suitable only for interior walls where dampness does not prevail.

Wood Stains and Fillers.—Practically all the wood used in cabinetmaking (furniture) or in finishing the interior of buildings is stained in some manner, either to augment its natural beauty

or to cause it to assume the appearance of a more valuable wood. The staining materials include a great variety of substances. Organic dyes, both of vegetable and coal-tar origin, acids, alkalies, metallic salts, and mineral pigments are used. The stains are usually classified according to the solvent or vehicle with which they are applied, as water, spirit, acid, and oil stains.

Water stains are the most used. The advantages of water as a solvent are its low cost and the ease with which it may be applied, but water causes the fibers of the wood to rise. This produces a roughened surface and necessitates refinishing. It is said that the raising of the fiber may be minimized by the addition of a small quantity of glycerin to the water. The water stains may consist of solutions of the aniline dyes or of water extractions of logwood, Brazil wood, madder, gall nuts, etc. The colors of these materials may be modified or changed entirely by the action of alkalies or acids. The aniline dyes are quite susceptible to the action of the substances contained in the wood, especially the tannic acid. The action will be most noticeable, of course, on those woods rich in tannic acid, such as oaks.

Spirit stains are preparations made by dissolving the coloring materials such as the aniline dyes and other materials in alcohol or in a good spirit varnish. Spirit stains dry very rapidly—so rapidly that it is difficult to apply them properly. The spirit stain may "bleed" also, *i.e.*, it may come through the varnish coat because of the dissolving action of the oil or solvent contained in the varnish. This difficulty may be overcome by selecting a dye that is soluble in some solvent as nitrobenzene, petroleum spirit, amyl acetate, acetone, or other liquid not contained in the varnish that is being applied. Many dyes of the various colors are obtainable, the solubilities of which are entirely different, so that they may be chosen with this point in view. All solutions of spirit stains must be clear without sediment or excess crystals. This is important because colors are frequently produced by the dye manufacturer by mixing two or more distinct dyestuffs. It may be that one of these dyestuffs will be soluble in the solvent chosen and the other not, so that if it be not all dissolved the true value of the dye will not be secured. To fix stains after the manner of a mordant in dyeing cloth, there may be applied after the stain has dried about a 5 per cent solution of alum or ferrous sulfate.

Acid stains comprise a great variety of substances. In this connection, the term "acid" is often employed to designate many

materials that are not acids in any sense. It includes the true acids such as sulfuric, nitric, and picric; salts such as alum, ferrous sulfate or copperas, potassium chromate and dichromate, potassium permanganate, sodium and potassium carbonate; and even the alkalies, sodium and potassium hydroxide themselves.

Wood may be "aged" by the direct application of ammonium hydroxide or by allowing the wood to stand in chambers containing vessels of ammonium hydroxide from which the ammonia gas may arise and act upon the wood. Oak is especially susceptible to this action; the product is known as *fumed oak*. This treatment with ammonia is useful only with those woods containing considerable gallic or tannic acids, since the color is dependent upon the formation of the ammonium compound of these substances.

Oil stains do not penetrate deeply and are most suitable for woods that are not to be filled. The oil used in the stain, when dried, partly fills the pores of the wood so that proper filling with a suitable filler cannot be accomplished. The oil stains are prepared by adding mineral pigments, such as burnt sienna, umber, or chrome yellow, to the oils, together with turpentine and some japan drier. Colors produced by oil stains are less clear and transparent than those produced by acid stains.

Wood fillers are used to close the pores in open-grained woods. If not filled, capillary action would occur in the pores and produce "sinking of the varnish." There are two kinds: paste and liquid fillers.

Paste Fillers.—The best grade of paste fillers consists of silica or barytes, boiled oil, and japan drier. Both silica and barytes become practically transparent in oil (page 552) and so produce a transparent filling. Fillers of poorer quality consist of cornstarch, whiting, boiled oil, turpentine, and drier. Such fillers have a tendency to shrink after drying, especially if made of the starch, thereby defeating the object for which the filler was applied. If intended to produce some color effect, the filler may also contain a coloring matter. The paste fillers are used in conjunction with the liquid fillers that are applied subsequently. The oaks, the walnuts, mahogany, ash, chestnut, and red gum are open-grained woods, and are filled with either paste or liquid fillers.

Liquid fillers consist of practically the same materials as the paste fillers, but in liquid fillers the liquid constituents preponderate. Liquid fillers are used only on close-grained woods, as cherry and birch. When fillers are used in conjunction with stains,

the filler must be applied after the stain. If the filler contains whiting or marble dust, and the stain is an acid stain, then a thin coating of shellac should be applied over the stain before filling to prevent the acid from acting on the calcium carbonate of which these substances consist.

Putty usually consists of whiting and raw linseed oil kneaded together. It may also consist occasionally of whiting, lead carbonate, white clay, or other similar materials with linseed oil.

Paint Practices

As was mentioned at the beginning of this chapter, organic coatings are applied to a great variety of metallic and nonmetallic materials of construction for the purpose of decoration or protection against deterioration, or for both of these purposes. From the engineering point of view the use of coatings for protection is most important, but the durability of a decorative coating obviously also is important. In the selection of the proper protective coating for a given application the following factors must be considered: (1) the chemical composition and the physical characteristics of the surface to be coated, (2) the environment to which the coated material is to be exposed, (3) the cost of the coating material and the cost of applying the coating, (4) the cost of replacement of the structure proper. All these items can be summarized by saying that the engineer must select his materials of construction, his methods of fabrication, and his protective coatings so that the finished structure will fulfill its intended function at the lowest possible cost per year.

Protective Coatings on Wood.—Wood surfaces vary according to species; even in the same species the climatic conditions cause differences in different parts of the same tree. Generally speaking, the wood surface should be penetrated somewhat by an applied coating for anchorage of the film. Formerly, the idea was held that the deeper the penetration the better the coating; for this reason, priming coats were used containing a high percentage of vehicle and a very low percentage of pigment. The pigment, often yellow ocher, had little covering power and gave little protection. Wood is not porous in the sense that it is made up of a continuous connecting cellular structure; it is more like a honeycomb of separate cells. The vehicle therefore penetrates only for a certain distance between cells and not through the cells themselves.

Realization of this fact has resulted in using as a primer a regular outside paint that has been thinned down somewhat more than is the practice in applying second coats.

The denser the wood, the less the adherence. In the same species, the spring wood, which is about one-third as dense as the summer wood, will take a better coat. Paint coatings always last longer on edge grain than on flat grain, particularly if the sapwood side is used. Some woods, like the pines, that have a high resin content, tend to show through after painting; this is called "bleeding." The use of an aluminum paint primer, on account of the lamellar structure of the pigment, is the best remedy for this defect. With most other soft woods, outside whites are good first coats.

Hardwoods are used almost solely for interior finishing and, being protected, are simpler to paint. An exception should be made in the case of flooring where coatings must withstand hard wear. If flooring is of softwood, it usually is coated with a hard durable varnish or enamel paint; these coatings, however, are very susceptible to marking. Hardwood floors (oak or maple) are usually finished by applying as many coats of a "sealer" as the surface will take without showing gloss; these are followed by a wax coating. With such treatment the wood is well waterproofed and, if the wax coating is occasionally renewed, it will withstand wear exceptionally well. Floor sealers are special varnishes, usually containing a synthetic resin vehicle.

Protective Coatings on Metals.—As has been mentioned in Chap. X, metals and alloys may be protected in many corrosive environments by the application of coatings of other metals or in some instances inorganic compounds (*e.g.*, vitreous enamels, "anodizing," etc.). In many circumstances, however, organic protective coatings, either alone or in conjunction with metallic and inorganic coatings, prove more economical than other means of protection.

In the application of organic coatings on metals, a different set of conditions is encountered than on wood. On the latter, coating adherence is due largely to the rough fibrous surface structure, whereas with metals, the surface is usually fairly smooth and nonabsorbent. The first or primer coat on metals must therefore be one that will adhere due to the operation of surface forces whose magnitudes are evidenced by the property called interfacial tension. With metal surfaces that have been roughened, a coating of lower adherence will be satisfactory as a primer. The

constituents of organic coatings that usually are responsible for adherence to metal are gums, resins, and tung oil.

For coatings that are to give protection against corrosion, it is highly desirable to use a paint, at least for the primer coat, that contains pigments inhibitive (page 554) in nature. The pigments that seem definitely inhibitive when used in primer coats on iron and steel are red lead, red lead plus litharge, zinc dust, zinc oxide, powdered lead alloy (page 559), sublimed blue lead, zinc chromate, and basic lead chromate. Many of these pigments when mixed in only small amounts with other pigments will provide satisfactory inhibitive action. For example, a very effective rust-preventive paint contains as pigments, iron oxide (preferably the natural oxide), a small amount of manganese dioxide, and about 2 per cent of zinc chromate. A coating of this pigment in linseed-resin vehicle has been shown to be as effective as a galvanized coating on fence wire. It can be applied directly on rusted surfaces from which any loose scale has been removed, and no rusting will occur during the life of the film, which is from 2 to 3 years. One of the authors has on exposure at present some 120 sq. ft. of screening which has had no other treatment than an application every three years of a thin coat of the above paint. This screening is now in its twenty-seventh year of exposure under conditions of high humidity and temperatures ranging from 0 to 95°F.

In most cases, careful cleaning of the metal surface before coating is an important part in the application of organic coatings as in the application of metallic and inorganic coatings (page 445). After cleaning, the surface may be given a special chemical treatment to produce an adherent passivating film of surface compound such as oxide or phosphate. It also is recommended that the surface should be free of condensed moisture when coatings are applied. Assuming that the surface has been properly prepared, most authorities would then recommend the application of a primer coat containing an inhibitive pigment, to be followed, when the primer coat has dried, by one or more coats of a paint that will produce a quite impermeable, durable film.

Coatings on Plaster and Concrete.—Plaster and concrete contain basic lime compounds, which in the presence of moisture are reactive toward many oil paints. If the surfaces are allowed to dry several months before the application of paint, there are several paint compositions that may be expected to give fairly satisfactory service. "Flat" paints, which usually are relatively high in pigment

content, are more likely to peel and scale than paints containing less pigment. It is recommended that plaster and concrete surfaces be treated with an aqueous solution of zinc sulfate (2 to 3 oz. of zinc sulfate per gallon of water) before painting. If this is followed by a primer coat of tung oil flat paint, thinned with tung oil, and a second coat containing the desired color in a tung oil vehicle, a satisfactory, quite durable coating will be obtained.

Another satisfactory coating for concrete floors is said to be obtained by first hardening the surface by applying aqueous solutions of magnesium fluosilicate, sodium silicate, and zinc sulfate; this treatment is followed by one or more coats of hard-drying varnish, pigmented with an abrasion-resisting pigment.

Light- and Heat-reflecting Properties of Coatings.—In the selection of paints for the exteriors of buildings, gasoline storage tanks, and similar structures, the heat-reflecting properties of various coatings become important. For painting the interiors of buildings, traffic signals, and other devices that should have a high visibility, the light-reflecting power of the coating is an important characteristic.

The percentage of incident light reflected from a surface will depend upon its chemical composition. Reflection from a surface may be regular (specular), *i.e.*, with a definite angle of reflection equal to the angle of incidence, or it may be scattered at all angles (diffuse). The first type of reflection is obtained from smooth, glossy, or polished surfaces such as those on metal mirrors, and to a considerable extent from varnishes and enamels. The second type, or diffuse reflection, is obtained from highly irregular surfaces and those coated with amorphous powders such as the pigments that have already been described. The almost pure white surface of magnesia is frequently taken as a standard of high percentage diffuse reflection. Obviously the flat wall paints are superior to glossy coatings containing the same pigments in respect to the diffusivity of the reflected light. Granting that one has the physical characteristics in a coating that will reflect light diffusely, the percentage of light reflected remains an important property. Various tests indicate that for visible light, white pigments are the best reflectors; these are followed by pigments of other colors in the following order: light cream, light pink, ivory, light yellow, light blue, light green, light gray, aluminum, medium green, dark red, dark green, dark blue, and black. The amount of reflection with a true black is, of course, practically nil.

For reflecting longer wave-length radiation, called infrared or heat radiation, the various coatings do not stand in the same order of efficiency as for reflecting visible light. White paints, however, still show the highest and black paints the least reflecting power. Aluminum paints have been widely used for this purpose but tests indicate that they are somewhat inferior to whites; for example, in one test, evaporation losses from three gasoline storage tanks were compared; one tank was painted black, one with aluminum paint, and one with white paint. The volatilization losses stood in the ratio 3.5:2.0:1.7, respectively.

The discussion of organic protective coatings should not be concluded without emphasizing the complexity of the subject. This is due not only to the fact that an almost infinite variety of coatings is available, but also because situations are constantly being encountered that involve materials of construction, operating conditions, and corrosive environments in combinations that lie outside the experience of the past. For their solution, many protective coating problems require close cooperation among coating technologists, designing engineers, and corrosion experts. It is hoped that this chapter will give the nonexpert an idea of the types of coatings that are available and a sufficient background in the subject so that he can understand and work with the specialists.

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CHAPTER XX

GLUES AND ADHESIVES

By Paul Fugassi, Ph.D.

Glues are substances which, with suitable solvents, form viscous solutions that ultimately change to solids possessing high cohesive and adhesive strength. In a popular sense glues are identified with the materials prepared by boiling suitably prepared hide, bones, and other animal waste matter with water. However, some types of glue can be prepared from nonanimal sources and some types do not use water for the solvent.

Glues as Colloids.—If a piece of animal glue is placed in warm water, the solid glue disappears and an apparently homogeneous mixture of glue and water is obtained. The glue-water mixture and mixtures of like properties are known as colloidal solutions.

All types of solutions may be classified as either molecular or colloidal. In molecular solutions the particles of solute present in the liquid are of molecular dimensions. Various types of molecular solutions are known. The solute may exist in molecular dispersions as in solutions of sugar in water, in ionic dispersions as in solutions of strong electrolytes (sodium chloride) in water, in molecular and ionic dispersions as in solutions of weak electrolytes (acetic acid) in water, or in molecular and associated molecular dispersion as in solutions of organic acids (acetic acid) in benzene.

In colloidal solutions, which are also called *sols*, the particles of solute dispersed in the liquid are larger than molecular dimensions and consist of many molecules held together either by primary valence forces or by secondary cohesive forces of the type normally present in solids. Colloidal solutions may be classified as either *lyophilic* or *lyophobic*. Lyophilic colloids are sometimes called natural colloids. The corresponding term for lyophobic colloids is artificial colloids. The basis for the nomenclature, natural or artificial, is the fact that lyophilic sols may be prepared by direct mixing of the solid and the liquid such as glue and water, whereas lyophobic sols cannot be prepared by direct mixing but must be

made indirectly such as the reduction of gold ions in water to form a sol of metallic gold in water.

Several methods are available for differentiating between molecular and colloidal solutions. In molecular solutions the solute diffuses very rapidly through parchment or other porous membranes. The diffusion of the solute in colloidal solutions through the same type of membrane is very slow. Molecular solutions show a very small *Tyndall effect;* colloidal solutions have a very marked Tyndall effect. The term, Tyndall effect, is used for the scattering of light at right angles to the path of the beam of light incident on the solution so that the position of the beam passing through the solution is clearly visible.

Gels.—Solid animal glue when mixed with warm water forms a lyophilic colloid. If sufficient glue has been used, cooling of the sol will result in the formation of a solid, jellylike mass called a *gel.* The formation of a gel is called *gelation*, which is a characteristic property of lyophilic sols. For some types of sols gelation results when the sol is heated. Gelation may also be caused by the addition of suitable electrolytes to the sol, and also through removal of the solvent by evaporation, adsorption, etc.

Physically, a gel is a two-phase system but the nature of the phases is in doubt. The amount of liquid present in the gel may be varied over wide limits. Gels may be prepared which contain as much as 99 per cent by weight of solvent. The strength of a gel depends to a great extent on the amount of solvent used in its preparation. Gels that contain large quantities of solvent are soft and flabby. If the solvent content is low, the gel will be hard and firm.

Gels made with glue or gelatin and water are called reversible gels because either the sol or the gel state can be obtained at will by heating or cooling the system. Irreversible gels such as the silicic acid gels cannot be reconverted into sols once they are formed. The term, reversible, as applied to a gel does not mean that the sol obtained by liquefaction of a gel possesses the same properties as the original sol from which the gel was obtained. Frequent liquefaction of a gel will decrease the gelation tendency of the resulting sol.

Glue or gelatin gels may be made less reversible to the action of water by the addition of small amounts of formaldehyde, tannin, alum, and other substances. Chromium salts in the gel on exposure

to light have the same effect. The behavior of formaldehyde is of importance in the preparation of water-resistant glues.

Classification of Glue.—A convenient classification for glues, due to F. W. Browne, is based on the methods employed to cause gelation. Gels may be formed in the following manner:

1. Cooling of a lyophilic sol. Animal glues such as hide or bone belong in this classification.
2. Heating of a lyophilic sol. Albumin glues obtained from blood and egg albumin are of this type.
3. Chemical reaction between the sol and some added substance. In casein sols the addition of calcium hydroxide to the sol will cause gelation. Formaldehyde has a similar effect on animal glues.
4. Evaporation of solvent. "Liquid glues," mucilage, sodium silicate, and other common adhesives are in this classification.
5. Direct chemical reaction leading to polymer formation. Phenol aldehyde condensation products which are sometimes used as glues are of this type. In order that the reaction take place in a reasonable time, glues of this type must be heated.

It is to be emphasized that, for a given glue, gelation may occur by several methods under conditions of actual use. When animal glue is used on wood, gelation results from lowering of the temperature of the sol, and animal glue is listed in class 1. However, loss of water from the sol by evaporation and through adsorption by the wood aids in the gelation process. These other effects are considered to be minor in comparison to the temperature effect for animal glues.

In another system of classification we might list glues on the basis of their principal chemical constituent. Thus we might speak of gelatin glue, casein glue, dextrin glue, etc. Unfortunately, the exact structures of gelatin, casein, etc., are not known. However, for the limited discussion to be given in this chapter, this second classification will be used.

Gelatin.—The principal component of animal and fish glue is gelatin, or closely related degradation products of gelatin. Gelatin is a member of a general class of compounds called proteins. A protein is a complex, organic compound that contains carbon, hydrogen, nitrogen, oxygen, and may contain sulfur and phosphorus. All proteins are thought to have the peptide type of link, R—CONH—R, between the various constituent groups in the compound. Proteins are very complex compounds whose chemical structures have not been determined. Part of the diffi-

culty experienced in the determination of the structure is due to the fact that gelatin reacts very readily with water to yield a variety of degradation products. Hydrolysis of gelatin in the presence of hydrochloric acid yields a large number of amino acids which are organic acids containing one or more $—NH_2$ or $=NH$ groups.

In a gelatin sol it is not known whether the dispersed particle consists of one large molecule or of a combination of molecules. The dispersed particle is thought to be large, but its "particle weight" is not known with certainty. The particle weight of a colloid is the weight of 6.02×10^{23} colloidal particles relative to the value of 32 taken for the weight of the same number of oxygen molecules. It is difficult to make significant particle weight measurements as the values obtained depend to some extent on the source material, on the method used to prepare the sol, and on the previous treatment of the sol. Estimated particle weights for various gelatin sols range from 700 to 100,000. The current view is that the higher values are more valid.

Gelatin glues may be classified on the basis of the stock used in the preparation. We can distinguish between four types of gelatin glues: (1) hide glue, (2) bone glue, (3) sinew glue, (4) fish glue.

For hide glues various hide trimmings are used together with discarded rawhide articles such as moccasins, loom pickers, and wrappers. Leather waste and discarded leather articles may be used only if the tanning agent present in the leather is removed. For bone glue, the source materials consist of fish bone from packing houses, garbage bone, butchers' refuse bone, horn pitch, dried bone of various types, bone trimmings from button manufacturers, and acidulated bone which is bone treated with acid to remove calcium salts. In the manufacture of sinew glue, green sinews from local stock and imported dried sinews are used. Fish glues are made from heads, bones, and other offal. Commercially, fish glues are classified as (1) head glue, (2) bone glue, (3) skin glue. Of these three types of fish glue, head glue is the strongest and the most valuable.

Gelatin Glue Technology.—The technology of glue manufacture consists of four steps: (1) preparation of stock, (2) formation of the glue solution, (3) purification and concentration of glue solution, (4) formation of solid glue.

Preparation of Stock.—For hide and sinew glues, the stock is first washed with water. This preliminary washing removes

dirt. With dried materials it softens and swells the stock; with salted stock it removes the salt. Following the washing, the stock is limed. In this operation the washed stock is placed in wooden or cement tanks, and covered with a saturated solution of lime in water. The stock is stirred occasionally and fresh limewater is added as needed. The liming operation may take from 2 to 30 days depending on the thickness of the stock. This period may be shortened by cutting the stock into small pieces. In the liming process, the hair and the fleshy part of the stock are removed, the stock swells, and mucin is extracted. After the liming is completed, the stock is washed free from lime and lime salts. Sometimes a small quantity of acid is added to the wash water to ensure that the stock is acid, as an acid stock is not subject to appreciable bacterial action.

For bone glues the stock is usually sorted to remove metallic and other impurities, and the bones are crushed to a fine meal. The bone meal is freed from grease by extraction with organic solvents such as benzene or carbon tetrachloride. Sometimes a portion of the grease is removed by preliminary steaming. The degreased bone meal is treated with a dilute aqueous solution (2 to 5 per cent) of hydrochloric acid for periods of 2 to 10 days. The acid solution leaches out $Ca_3(PO_4)_2$ present in the bone, forming a solution of phosphoric acid and soluble calcium phosphate salts. Separate treatment of the acid wash water with lime yields $Ca_2H_2(PO_4)_2$, "precipitated bone phosphate," which is used as a fertilizer and in the manufacture of bone china. After extraction of $Ca_3(PO_4)_2$, about 33 per cent of the original bone is left. The residue is a soft, cartilaginous mass called collagen, which, after washing and neutralization of any remaining acid, may be converted into glue or gelatin. If the collagen is dried at low temperatures, it yields commercial ossein.

For fish glue, the preliminary washing with water removes dirt and blood from fresh fish offal and salt from salt fish offal. No further treatment is needed before the extraction of the glue.

Extraction of Glue.—After suitable preparation, the stock is placed in a kettle or pressure vessel, water is added, and the mixture heated. In general, pressure tanks are used for bone stocks. The treatment with hot water is probably a hydrolysis, as glue is not present in the stock as such. However, the exact nature of the reaction is not known. For a given portion of stock the extraction

may be carried out in one operation or in several successive operations. If successive extractions are used, the first extraction is done with the smallest amount of water and the lowest possible temperature (70°C.). The extraction is made for periods of 2 to 6 hr. and is terminated when a sample of the liquid solidifies. The liquid is removed and a fresh portion of water added. The second extraction usually takes a longer time and is done at a higher temperature. Extractions are continued until, for the last one, boiling water is used. The liquid from the end extractions contains relatively little glue, does not solidify on cooling, and must be concentrated before the glue may be removed. The best grade of glue is obtained from the first extraction. The remaining extractions yield progressively poorer grades of glue.

In the course of the extractions most of the grease remaining in the stock rises to the surface and is removed by skimming the surface. The residue in the kettle is used for fertilizer and may contain an appreciable amount of insoluble salts of calcium and various fatty acids. If desired, these acids may be recovered by treatment of the residue with sulfuric acid.

Treatment of Glue Solution.—The solution of glue in water is sometimes filtered under pressure to remove relatively coarse foreign matter. To obtain very clear glues, alum is added to the hot solution and the resulting precipitate of aluminum hydroxide eventually carries down in a precipitate most of the finely divided foreign matter in the glue. However, in this clarification procedure, the extended heating of the solution results in hydrolysis of some of the glue so that a glue of lower strength is obtained.

Sometimes the glue is bleached to obtain a light-colored product. Sulfur dioxide or its aqueous solutions are the bleaching agents most commonly used. Glue is an excellent bacterial food and some preservative must be added to prevent putrefaction. Sulfur dioxide if used as a bleach also serves as an antiseptic. Boric acid, borax, bisulphites, and traces of formaldehyde are also used as antiseptics.

The glue solutions resulting from the first and second extractions usually gel on cooling of the solution. Liquid from subsequent extractions must usually be concentrated by evaporation of some of the water. The evaporation is usually done by flowing a thin film of the glue solution over heated metal surfaces. In this manner the time required for evaporation is lowered and excessive degradation of the glue by hydrolysis is avoided.

Formation of Solid Glues.—The glue-water solutions are placed in shallow iron pans and allowed to set. The resulting gel is removed from the pans and sliced horizontally into thin slabs. The sections from the top and bottom contain most of the grease and sediment, and are usually segregated for the preparation of cheaper grades of glue. The remaining sections are placed on a drying net over which warm air is circulated. The drying operation may continue for a week. The gel on drying is in the form of slabs and may be packed as such or it may be ground to give flake or powdered glue.

Commercial Forms of Gelatin Glue.—Gelatin glues are marketed as solids in the form of cakes, flakes, or powder. Most fish glues are sold as thick viscous liquids but solid fish glues are available although they are hygroscopic. Glues are frequently described in such a manner as to indicate the source from which they were prepared; *i.e.*, hide glue, bone glue, etc. Certain special forms having special names are also available.

Opaque, or Russian, glue is glue to which a white, inert powder has been added. Barium sulfate, zinc oxide, talc, and white lead are the more common adulterants used in opaque glues. The effect of the powder, if any, is to weaken the glue. Hide glue, bleached to a light color with bleaching powder, is marketed as Cologne glue. Gilder's glue is a bleached skin glue which is prepared from the first extractions only and is difficult to dissolve. Paris glue is the term applied to glue that has been intentionally heated for a long time so as to have very little adhesive strength. Isinglass is a fish glue prepared from the sound or swim bladder of certain species of fish such as sturgeon, carp, and hake. Isinglass is nearly pure collagen and is easily converted into gelatin by treatment with hot water. Gels of isinglass and water are very strong. Liquid glues are fish glues or weak animal glues to which has been added some acid such as acetic, formic, boric, nitric, or salicylic. The function of the acid is to prevent gelation of the glue at room temperatures. Salts such as zinc sulfate may be added to liquid glue preparations for the same purpose. Elastic glue or flexible glue consists of equal parts by weight of glycerin and glue. It remains permanently elastic and soft and is used in bookbinding.

Grades of Glues.—After preparation, glue must be classified and graded. The grading of glue is a difficult matter and is usually done on a relative basis by comparison of the given sample with accepted standards. In making such comparisons chemical tests

are of little value and the chief reliance is placed upon various physical tests. A large number of physical tests have been devised. Two of the more important physical tests are (1) viscosity of the glue-water solutions, and (2) strength of the gel resulting from the glue-water solution. In the last analysis the value of a glue depends mainly on the strength of the gel obtained with its use. However other factors such as the covering power, *i.e.*, the weight of glue required for a gel of given strength, are of importance. For certain uses such characteristics as foaming tendency, presence of grease, odor, and keeping qualities, are of prime importance. For example, glue used in paper manufacture must be free from grease. In the manufacture of wood veneers the glue solution is applied with rotary brushes. If the glue foams excessively on application, a large number of air bubbles will be present in the gel between the veneer and the base wood. Such veneer joints will be weak and the veneer might eventually split away from the base wood.

Many systems of standards for glue classification have been proposed in recent years. However the one in greatest use is the series established by Peter Cooper over a century ago. In this system, glues are graded in eleven classes, in order of decreasing strength, as A Extra, 1 Extra, 1, 1 x(one cross), 1¼, 1⅜, 1½, 1⅝, 1¾, 1⅞, and 2. The significance of the designation applied to each class is not known but it is thought to have been the distance through which a certain weighed rule compressed the gel prepared from an aqueous glue solution of known concentration. The Cooper series is not complete as commercial glues can be obtained of greater strength than A Extra. Although the origin of the Cooper standards was probably based on gel strength, the comparison between the glue sample and the standards is not limited at the present time to the determination of gel strength.

Glue Testing.—Consumers generally test each lot of glue purchased to make certain of its suitability for the purposes intended. Chemical analysis of a glue is difficult and the results from such analyses are difficult to interpret. Tests on a given sample are primarily physical and may be classified under three headings: (1) examination of dry glue, (2) physical properties of a glue-water solution of known concentration, (3) physical properties of a gel prepared from a solution of known concentration.

Examination of Dry Glue.—The cut of a glue may give some indication of its quality. A thin cut glue usually indicates high

quality. Thin cut glues are made from gels that contain a large percentage of water. The sections from the gel are sliced in thickness of 1/4 to 1/2 in., so that after drying the sections shrink to a thickness of about 1/16 in. Thin sections cannot be cut directly from concentrated gels as the sections would curl badly. Only very good glues can form gels containing a large percentage of water, which are sufficiently solid to be sliced.

A thin cut glue that is flexible enough to be bent into the shape of a U is a good glue. However water present in the glue increases the flexibility. This fact should be remembered.

Examination of the fracture obtained by breaking a piece of solid glue may yield useful information. If the fracture is splintery, the glue is strong. If the fracture is glassy or vitreous, the glue is brittle and has a lower strength. Bone glues usually give a glassy fracture. Overheated glues also show a similar type of fracture.

The surface of a piece of solid glue should be free from bubbles. Bubbles are considered to be evidence of putrefaction which began in the glue solution and continued in the gel during the drying operation. Confirmatory evidence for putrefaction can be obtained by moistening the glue and noting the odor. Glue that shows evidence of putrefaction is probably a low grade of glue as putrefaction decreases its strength and also indicates lack of precaution in the manufacture.

Ground glues are frequently blended to give gels of the proper strength or to reduce the price of glue. Close visual inspection will show whether the powder is uniform or is a mixture. If the glue is coarsely ground, only particles of about the same size should be compared as the smaller particles might appear to have a lighter color because of their smaller size.

Examination of Glue Solution.—In the preparation of a glue-water solution a known weight (10 to 25 g.) of glue should be broken into small pieces, placed in a suitable receptacle, and covered with a known volume (100 cc.) of water. The mixture is allowed to stand at room temperature until the glue is thoroughly softened. After softening, the mixture is heated to 80°C. and stirred from time to time so that all of the solid is dispersed. The glue-water solution should be heated in a water bath to prevent localized superheating and care should be taken that the temperature does not exceed 80°C. Overheating of glue solutions accelerates hydrolysis of gelatin and results in a weaker glue. In general, several solutions

of the same sample are prepared at the same time together with solutions of the standard glues.

Odor.—The odor of the solution will vary according to the stock from which the glue was made. Evidences of putrefaction should be absent. An earthy smell indicates that the glue was made from an overlimed stock. In some cases the odor might be due to preservatives added to the glue and in other cases to essential oils, such as wintergreen, which have been added to mask the odor.

Acidity and Alkalinity.—Glue solutions when tested with litmus are usually acidic or basic. Neutral glues are very rarely found. Bleaching with sulphur dioxide, correction of overliming, or use of acid in the preparation of stock as in bone glues will cause the glue to be acidic. Glues made from overlimed stock will be alkaline.

Viscosity.—By relative viscosity one means the rate of flow of a liquid through a given opening under a given pressure head and at a given temperature, relative to the rate of flow of a standard liquid, such as pure water, under the same conditions. In comparing a series of glue solutions that contain the same weight concentration of glue, the solution of the best glue will have the highest viscosity. Viscosity determinations are usually made at temperatures sufficiently high (35 to 65°C.) so that gelation will not occur.

The determination of viscosity is of great value in the grading of glues but is not sufficient in itself. Acid-treated bone glues usually run lower in viscosity than would be expected from their value as determined by other tests. Glues clarified with alum run high in viscosity; glues in which alum is not used as the clarifying agent run low in viscosity.

Grease.—To a portion of the glue solution, a small amount of lampblack is added and the mixture stirred thoroughly. The solution is painted on white paper with a small brush. If grease is present the painted paper will not be uniformly black, but a number of small, white spots will be present. The amount of grease in the glue will be roughly proportional to the number of spots. Quantitatively, grease may be determined by treating a sample of solid glue with water and dilute hydrochloric acid to decompose any salts of fatty acids and then extracting the grease from the mixture with benzene. For some uses such as in the manufacture of paper, grease should not be present.

Foam.—After agitation by shaking or vigorous stirring, the quantity of foam—estimated volume of foam as compared to the

volume of the solution—is determined. The stability of the foam should be noted. In glues that contain grease the foam usually disappears rapidly. Excessive foaming in a glue might be due to excessive acidity or alkalinity, overheating in the extraction process, or insufficient liming.

Examination of the Gel. *Comparative Set.*—The solutions of the various glue samples are removed from the water bath and placed in a location sheltered from drafts so that they cool uniformly. The solutions of the better glues usually gel first.

Gel Strength.—After gelation the gels are arranged in order of their strength. The strength of the gel may be measured by its resistance to the pressure of the finger, or by some mechanical method such as plungers weighted with lead shot. The quality of a given glue is directly proportional to the gel strength. The better glues make the stronger gels.

Shear Test.—For glues used in the joining of wood the best test for a given sample is to make test joints and determine their strength. Maple or walnut blocks are usually employed but at times porcelain blocks have been used. The strength of the joint is determined by measurement of the force required to shear the joint using a loading machine. For a given glue sample five or six joints are prepared and their average strength is taken as characteristic of the glue. In making tests of this type it has been found that the strength of a glued joint depends on the joining pressure applied to the two blocks when the joint is made. Low joining pressure gives erratic results. The exact value of the joining pressure to be used depends on the nature of the wood and the viscosity of the glue solution. Glues with low viscosities do not require high joining pressures. The upper limit for a joining pressure is obviously dependent on the strength of the wood being joined. Joining pressures that would crush the wood cannot be used in preparation of the joint. After preparation, the joints are usually allowed to dry for a week before being tested.

Selection of Glue for Wood Joints.—Under the Cooper standards, glues above grade 1⅜ are suitable for wood joints. In many cases the strength of the joint will be greater than the strength of the woods joined together. Low viscosity is a desirable characteristic for glues used in wood joints, as the extent of permeation of glue into the wood depends on the viscosity of the glue solution. The importance of the joining pressure has been previously mentioned.

Casein Glues

Casein.—Casein is a phosphoprotein, *i.e.*, one which under suitable conditions hydrolyzes to yield organic acids containing phosphorus.

The principal source of casein is cows' milk. Casein is a by-product of the dairy industry and is obtained from skimmed (fat-free) milk. Casein can be precipitated as a curd by the addition of acid to skimmed milk or by the action of bacteria or enzymes. The curd is washed, pressed, and dried. As a commercial product casein is a white powder which is not hygroscopic. It is acidic and is insoluble in water, alcohol, and most organic solvents. Casein can be colloidally dispersed in alkaline aqueous solutions. In the alkaline solution, it is assumed that salts called "caseinates" are formed. However, the evidence for definite compound formation between casein and various metallic ions is not conclusive and the properties of casein may be explained by purely physical phenomena. For the discussion to be given here, it will be assumed that "caseinates" actually exist.

In water the alkali metal caseinates (Li, Na, K, and NH_4 salts) give colloidal solutions which on evaporation of the water form gels. The caseinate gels have high cohesive and adhesive strength. Gels of the alkali metal caseinates are reversible and the colloidal solution may be reformed by addition of water to the gel. Aqueous colloidal solutions of the alkaline-earth metal caseinates (Ca, Ba, and Mg salts) also gel on the evaporation of the water but the gel so formed is irreversible, *i.e.*, on the addition of water to the gel, the colloidal solution is not reformed. Caseinates of the heavy metals also give irreversible gels.

Types of Casein Glues.—By taking advantage of the properties of casein two types of casein glues have been developed: (1) glues forming reversible gels, (2) glues forming irreversible gels. Those of the first type are employed for the same purposes as the gelatin glues. Glues of the second type are water resistant and are used where resistance to moisture is of paramount importance.

Reversible Casein Glue.—The alkali required to disperse casein in water can be introduced into the mixture in two ways: (1) by addition of sodium or ammonium hydroxide, (2) by addition of sodium or potassium salt of a weak acid. In some cases a portion of the sodium or ammonium hydroxide is replaced with calcium hydroxide. The addition ot a small amount of calcium hydroxide

renders the gelation less reversible but the gel obtained is not strictly impervious to the action of water.

According to F. W. Browne a suitable mixture for woodworkers' glue contains 100 g. of casein to 600 g. of water. The amount of alkali required is 0.1 equivalent of sodium hydroxide (4.0 g.) or 0.2 equivalent of ammonium hydroxide (13 cc. of 29 per cent "aqua ammonia"). If the alkali is furnished by a hydrolyzable salt, the equivalents of salt vary with the nature of the salt employed. A smaller amount of the salts of the weaker acids is required. For example with the previously mentioned mixture, 1.5 equivalents of sodium fluoride would be used as compared to 0.077 equivalents of borax.

The one important characteristic of the glue solution is the pH. In the mixtures just cited, the pH is kept under 10.5. At pH values greater than 10.5 the hydrolysis of casein proceeds rapidly and the products of hydrolysis weaken the adhesive power of the glue. In addition, the viscosity of the sol reaches a maximum around a pH of 9.2, and falls off at higher and lower pH values.

With strong bases like sodium hydroxide the correct amount of base must be used in the mixture to avoid thinning and decomposition of the sol. With ammonium hydroxide the thinning effect at the higher pH values is not too noticeable and the hydrolysis might be hindered by the presence of excess NH_3 which is one of the end products in the hydrolysis of casein. With salts of weak acids the amount of salt used can be varied somewhat without affecting too markedly the viscosity and the stability of the sol.

Reversible casein glues remain fluid and workable for long periods of time. However bacterial action and hydrolysis eventually cause thinning of the sol and a loss in adhesive strength. Bacterial action may be reduced by use of a suitable antiseptic but there is no way of preventing hydrolysis.

In the preparation of casein glue, a known weight of casein is added to the correct amount of water and the mixture is stirred until the casein has become completely swollen. The soaking period will vary with the grade of casein used and the degree of fineness of the casein powder but will not exceed 15 min. The alkali is now added to the casein-water mixture and the resulting mixture stirred until the casein has gone into colloidal solution. The stirring period will range from 10 to 30 min. but will be some what shorter if warm water is used.

Reversible casein glues may be used for wood joints in place of gelatin glues. They are less expensive than gelatin glues and are very satisfactory. Casein glues, being strongly alkaline, tend to stain wood and produce a more noticeable glue line than gelatin glues.

Irreversible Casein Glues.—All commercial water-resistant casein glues use calcium hydroxide to produce an irreversible gelation. Calcium hydroxide is a cheap source of alkali and its limited solubility in water gives the low concentration of calcium ions needed in the preparation of the gel. Higher concentrations of calcium ion such as would be obtained by the addition of calcium chloride or some highly soluble salt to a casein-water dispersion cause the immediate precipitation of casein as an insoluble curd. With saturated aqueous solutions of calcium hydroxide the time required for gelation will be sufficiently long so that the glue may be used. Calcium salts such as calcium tartrate, with less solubility in water than calcium hydroxide and not too great an insolubility, require more time for formation of the irreversible gel.

An excellent casein-lime glue has the following composition: water, 300 g.; casein, 100 g.; calcium hydroxide, 16 g. (0.43 equivalents). The disadvantage of this particular mixture is that it sets in about 30 min. and the mixture must be used within that time. The working life of this particular formula may be increased by the addition of animal glue.

Since the working life of the mixture just mentioned is too short for most purposes, mixtures are usually employed that are more alkaline and have a longer setting period. The composition of a typical mixture is: water, 300 g.; casein, 100 g.; calcium hydroxide, 30 g. (0.81 equivalents); sodium salt of weak acid, 0.275 equivalents. Among the sodium salts that may be employed are tetraborates, phosphates, stannates, carbonates, and arsenates.

The use of sodium silicate in the form of an aqueous sol (water glass) as the source of the sodium salt changes the property of the glue mixture considerably. Mixtures with sodium silicate require less alkali for a given working life and this effect is probably due to the colloidal dispersion of sodium silicate. The lower alkalinity reduces the tendency of the casein to hydrolyze. A typical mix using sodium silicate is as follows: water, 300 g.; casein, 100 g.; calcium hydroxide, 20 to 30 g.; water glass, 70 g. (density = 40°Bé., 0.2 equivalents of Na_2O). In the preparation of this mixture the sodium silicate solution is added last.

Commercial Forms of Casein Glues.—Casein glues are sold either as "prepared" glues or as "wet-mix" glues. Prepared glues are dry powders to which only water must be added to obtain the glue solution. Wet-mix glues consist of two or three separate ingredients, which must be weighed and mixed with water to prepare the glue solution. Prepared glues are simpler to use and yield more consistent results. Wet-mix glues require accurate measurement of the ingredients for good results and are possibly somewhat cheaper than prepared glues. Glue mixtures using water glass cannot be marketed conveniently as prepared glues; for mixtures of this type wet-mix glues must be used.

Additional Adhesives

Albumin Glues.—Albumins are a type of protein that can be isolated from blood serum, egg white, certain seeds, and milk. The principal sources of albumin are blood serum and egg white. Albumins are soluble in water as colloidal dispersions. Such sols are neutral and gel when heated. The gelation of albumin sols is irreversible and the water-albumin gel makes an excellent water-resistant glue. Either egg or blood albumin may be used but blood albumin yields the better glue.

Sodium Silicate Glues.—Water glass is a colloidal dispersion of sodium silicate and silicon dioxide in water. Sodium silicate is obtained by the fusion of soda ash and sand in a suitable furnace. The fused product is cooled and dissolved in water. On loss of water, water glass yields a gel that has sufficient adhesive and cohesive properties to be used as a glue.

The principal use of sodium silicate glues is in the manufacture of cardboard and paper boxes and containers. Water glass glues adhere strongly to glass but are not resistant to water. As a glass cement, inert solids are usually added to the water glass to compensate for shrinkage of the gel on drying. Powdered solids such as asbestos, barium sulfate, talc, or Alundum cement are excellent for this purpose.

Mucilage.—Mucilage is the aqueous solution of a gum used as an adhesive. The term, gum, is applied to mixtures that cannot be crystallized; they contain carbohydrates, and on hydrolysis yield sugars. Mucilage does not give joints of high tensile strength and is used for stamps, envelopes, etc., where strength is not required. Gum arabic is obtained from the acacia tree and contains mixed mineral salts of arabic acid. Dextrin is prepared by heating starch

to 200 or 250°C. If the starch is moistened with a little nitric or hydrochloric acid, it need only be heated at 140 to 170°C. The dextrin prepared with acid has a lighter color. The principal component of present-day mucilage is dextrin although some gum arabic may be used. Pectin, a carbohydrate gelation agent, can be extracted from the cellulose structure of fruits and is the solidifying agent present in fruit jellies. The use of pectin as an adhesive has been suggested. Other vegetable gelation compounds have been isolated but have not attained extensive use. Aqueous solutions of pentosans (sugar molecules containing five carbon atoms) obtained by extraction from oat hulls and corncobs have been proposed as adhesives.

Resin Glue.—Resin was the term originally applied to various solid organic substances, vegetable in origin and insoluble in water, exuded by various plants. If the exuded substance is water soluble it is called a gum. In recent years the term resin has been applied to highly polymerized organic molecules that are insoluble in water. Solutions of resins in suitable solvents find some use as glues.

Rubber cement is rubber dispersed in benzene. If pitch has been added to the rubber-benzene sol, the mixture is called marine glue. Shellac, a resin of animal origin, dissolved in alcohol serves as an adhesive. Alkyd resins, which are polymerized molecules of glycerin-phthalic acid ester, when dissolved in acetone make an excellent glue. Bakelite cements, which on being heated yield formaldehyde-phenol condensation products, are commercially available. Other synthetic resins dispersed in suitable solvents are also used.

Nitrocellulose Glues.—Pyroxylin dissolved in acetone gives a film that adheres strongly to glass. Pyroxylin, a nitrated cellulose, is obtained by treating cellulose with nitric acid. Collodion is a solution of celluloid in alcohol and ether.

Gluten Glue.—Gluten is a protein present in wheat flour. The adhesive characteristic of flour paste made by mixing water and flour is due to the gluten content in flour. Japanese cement, which is used for fastening paper, is made by mixing rice flour with hot water.

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CHAPTER XXI

INSULATING MATERIALS

By Paul Fugassi, Ph.D.

The term, insulating materials, is applied to those substances which are used to retard the transfer of heat energy and prevent the conduction of electricity. The classification of materials as conductors or insulators is not a definite one. All substances conduct to some extent and whether a given substance is considered as a conductor or an insulator depends entirely on the particular application being considered.

Thermal Insulators

Heat energy can be transferred from one body to another by three different mechanisms: convection, conduction, and radiation.

Convection.—Convection is a mode of heat transfer in liquids or gases that results from the mixing of different portions of the liquid or gas. If the mixing is caused entirely by density changes resulting from temperature differences, the convection is said to be "free convection." If the mixing is mechanical, the convection is termed "forced convection." For insulating purposes forced convection is not usually important and will not be discussed.

Since the phenomena of free convection are difficult to investigate experimentally, the influence of the different variables is not known. The quantity of heat, q_{conv}, escaping in unit time from one solid plane surface to another parallel plane surface is given by the equation $q_{conv} = KA(T_2 - T_1)$, where K is a constant, A is the area, and $(T_2 - T_1)$ is the temperature difference between the two plates. The nature of K is complex as its numerical value for a given fluid depends on the density, the specific heat, the viscosity, and other characteristics of the fluid. K varies slightly with the temperature difference. Also involved in K is a factor dependent on the particular geometrical arrangement of the plates. The heat loss from a horizontal heated surface facing upward is much greater than for the same horizontal surface facing downward. The distance of separation of the two plates is also of importance. For air

at one atmosphere it has been shown that the heat transfer is independent of separation distances greater than 1 in., but increases rapidly with decreasing separation.

Conduction.—Conduction is a mode of heat transfer that does not involve the displacement of any portion of the substance through which conduction is taking place. Obviously conduction is the only method by which heat energy can flow through a nonporous solid. For liquids and gases conduction occurs simultaneously with convection unless special precautions are taken to eliminate mixing resulting from density differences. Conduction is a molecular phenomenon; rapidly moving molecules transfer their kinetic energy to other molecules that are moving slowly. Convection is a mass phenomenon; large numbers of molecules move en masse from one part of a substance to another as a result of density differences.

The quantity of heat, q_{cond}, transferred by conduction in unit time, is given by the equation, $q_{cond} = \frac{K'A(T_2 - T_1)}{L}$, where A is the cross-sectional area, $(T_2 - T_1)$ is the temperature difference, and L is the thickness. K' is a constant having a characteristic value for each substance and is called the coefficient of thermal conductivity. Considering any one given substance, the value of K' varies with the physical state of the substance. In general the values of K' for the liquid and solid states are comparable; the value of K' for the gaseous state is much smaller. Gases are always poorer conductors than liquids or solids.

For gases, K' is related to η, the coefficient of viscosity, and C_v, the specific heat at constant volume, by the equation $K' = \frac{5}{2}\eta C_v$. Conduction of heat through any gas is practically independent of the pressure of the gas over a moderate pressure range. Appreciable decrease in the conductivity results only when the pressure of the gas becomes sufficiently low so that the mean free path of the gas molecules is comparable in size to the thickness of the sample (L in the above equation). The mean free path of a gas molecule is the average distance traveled by the molecules between successive collisions. For this reason Dewar flasks must be evacuated to a very low gas pressure.

It can be shown that hydrogen and helium, the two lightest gases, should have by far the highest thermal conductivity. All other gases should have comparable conductivities. These predictions have been experimentally verified as shown in Table 92.

TABLE 92.—COEFFICIENTS OF THERMAL CONDUCTIVITY FOR GASES (0°C.) $\frac{\text{B.T.U.}}{(\text{Hr.})(\text{Ft.})(°\text{F.})}$

Molecule	K'	Molecule	K'
Hydrogen	0.0917	Air	0.0129
Helium	0.0758	Water (100°C.)	0.0126
Methane	0.0177	Ammonia	0.0116
Oxygen	0.0134	Ethane	0.0104
Nitrogen	0.0131	Carbon dioxide	0.0081

For liquids, the following equation has been suggested for K',

$$K' = 0.931 \left(\frac{C_v}{C_p}\right)^{1/2} \cdot \frac{3R}{N} \cdot \left(\frac{N}{V}\right)^{2/3} \cdot \mu$$

In this equation, C_v and C_p are the specific heats at constant volume and pressure, R is the gas constant, N is Avogadro's number, V is the molal volume, and μ is the velocity of sound in the liquid. Table 93 lists some experimental values. With the exception of mercury and water, liquids have comparable conductivities.

TABLE 93.—COEFFICIENTS OF THERMAL CONDUCTIVITIES FOR LIQUIDS (0°C.), $\frac{\text{B.T.U.}}{(\text{Hr.})(\text{Ft.})(°\text{F.})}$

Substance	K'	Substance	K'
Mercury	4.83	Aniline	0.104
Water	0.337	n-Amyl alcohol	0.083
Ethylene glycol	0.153	Carbon tetrachloride	0.064

The best solid conductors of heat are the metallic elements. The heat conductivity of metals generally parallels the electrical conductivity. Alloys usually have heat and electrical conductivities lying below those of the pure metal constituents. The value of K' for crystalline compounds can be qualitatively obtained from the equation $K' = \alpha\rho C_v$, where α is a constant which can be calculated from the physical characteristics of the substance, ρ is the density, and C_v is the specific heat at constant volume. The exact nature of α cannot be discussed here but it can be shown that it decreases with increase in the complexity of the lattice structure. For example, α decreases in going down the series: magnesium oxide, MgO; aluminum oxide, Al_2O_3; mullite, $3Al_2O_3 \cdot 2SiO_2$. Considering

α alone, magnesium oxide should be the best and mullite the poorest conductor of the three substances listed. Experimentally this has been found to be the case. It should be noted that crystalline substances with high densities and high specific heats are the best conductors. In the following table experimental conductivity coefficients are listed for metals and nonmetallic crystalline substances.

TABLE 94.—COEFFICIENTS OF THERMAL CONDUCTIVITY FOR SOLIDS (0°C.)
$\frac{\text{B.t.u.}}{(\text{Hr.})(\text{Ft.})(°\text{F.})}$

Substance	K'	Substance	K'
Silver	242	Quartz, ∥ to axis	7.9
Copper	224	Quartz, ⊥ to axis	4.2
Aluminum	117	Marble	1.9
Brass (70–30)	56	Gypsum	0.75
Nickel	36	Magnesia	0.35
Cast iron	29	Asbestos	0.06

Radiation.—Radiation is the term applied to heat transfer resulting from wave motion through space. The quantity of heat, q_{rad}, passing from one plane surface to another parallel plane surface, is given by the equation:

$$q_{rad}\ (\text{B.t.u. per hr.}) = 0.172 \times 10^{-8} A (T_1^4 - T_2^4) \cdot F_E.$$

In this equation A is the area, T_1 is the absolute temperature of the emitting surface, T_2 is the absolute temperature of the receiving surface, and F_E is an emissivity factor. For parallel plates F_E is evaluated by use of the equation:

$$F_E = \frac{1}{\frac{1}{P_1} + \frac{1}{P_2} - 1}$$

where P_1 and P_2 are the emissivities of the emitting and receiving surfaces.

The emissivity of a given surface depends not only on the chemical constitution but also upon the physical nature of the surface. Some generalizations may be made: (1) The emissivities of most nonmetal surfaces are high. (2) The emissivities of highly polished metals are low. (3) Emissivities increase with increase in temperature and with increase in the degree of roughness of the

surface. Some illustrative experimental data are listed in Tables 95, 96, and 97.

TABLE 95.—EFFECT OF SURFACE ROUGHNESS ON EMISSIVITY OF IRON

Surface	P	Temp., °F.	Surface	P	Temp., °F.
Highly polished	0.052	350	Ground sheet	0.550	1720
Highly polished	0.144	800	Rusted plate	0.612	68
Freshly emeried	0.242	68	Oxidized	0.736	212
Turned, cast	0.435	72	Iron oxide	0.85	930

TABLE 96.—EMISSIVITIES FOR VARIOUS METALS (HIGHLY POLISHED)

Metal	P	Temp., °F.	Metal	P	Temp., °F.
Mercury	0.120	212	Aluminum	0.039	440
Lead	0.075	440	Silver	0.020	440
Nickel	0.070	440	Copper	0.018	176
Platinum	0.054	440	Gold	0.018	440

TABLE 97.—EMISSIVITIES FOR VARIOUS NONMETALLIC SURFACES

Surface	P	Temp., °F.	Surface	P	Temp., °F.
Asbestos	0.96	74	Red brick	0.93	70
Ice	0.95	32	Plaster	0.91	72
Glass	0.94	72	Enamel (white)	0.90	66

Function of Insulation.—The purpose of insulation is to replace a short heat flow path of lower resistance by a longer path of higher resistance. As a consequence, the surface in contact with air will be at a lower temperature and the heat loss from the surface will be correspondingly decreased. In many cases the surface of the insulation may be covered with a metallic surface of low emissivity and the heat loss is diminished further. It is important to remember that the magnitude of the heat loss from any object is dependent on the surface area. Addition of an insulating cover increases the surface area and the lowering of the temperature gradient given by the insulator may be offset by the increase in area. This is particularly true for small objects such as pipes, where small changes in the radius cause a correspondingly large percentage of change in the surface area. It is actually possible under some condi-

tions to have greater heat loss from the insulated object than from the uninsulated object.

Properties of Insulators.—One of the most important characteristics of insulators is their thermal stability or their ability to withstand decomposition or physical changes for long periods of time at the temperatures where they are employed. Organic materials are usually limited to a maximum temperature of 100°C. Inorganic materials must be used for higher temperatures. If a smooth-surfaced metal is being used to decrease radiation loss, the surface must not oxidize or react, for in event that reaction takes place, a rough surface of some inorganic compound with a higher emissivity replaces the originally smooth surface of the metal. The physical properties of the insulation, such as strength, rigidity, physical state, and method of application, are important in the actual use of insulation in addition to the conductivity of the material.

Organic Insulators.—Organic insulators are naturally occurring materials which are distinguished by low apparent density indicating a highly porous substance. The insulation of such substances is due mainly to the small air pockets scattered throughout the material. A few of the commonly used substances are listed in Table 98. The listed conductivities vary with the apparent density.

TABLE 98.—HEAT CONDUCTIVITIES OF ORGANIC INSULATORS (25°C.)

Substance	K' B.t.u. per (hr.) (ft.) (°F.)	Density, lb. per cu. ft.
Wool	0.021	6.9
Cattle hair (felted)	0.022	11.0
Eelgrass	0.023	4.6
Cotton wool	0.024	5.0
Corkboard	0.025	10.0
Silk	0.026	6.3
Wood pulp	0.028	16.2
Sugar-cane fiber	0.028	13.2
Sawdust	0.034	21.0
Cardboard (corrugated)	0.037	
Paper	0.075	
Leather	0.092	62.4

Inorganic Insulators.—A large number of inorganic insulators are naturally occurring minerals; others are prepared materials. Some inorganic insulators are listed in Table 99.

TABLE 99.—HEAT CONDUCTIVITIES OF INORGANIC INSULATORS

Substance	T, °C.	K', B.t.u. per (hr.) (ft.) (°F.)	Density, lb. per cu. ft.
Air (still)	0	0.013	0.08
Slag wool	30	0.022	12.0
Mineral wool	30	0.023	9.4
Glass wool	25	0.024	4.0
Aluminum foil (7 air spaces)	38	0.025	
Diatomaceous earth (powder)	25	0.026	10.6
Charcoal (6 mesh)	25	0.031	15.2
Wood ashes	25	0.041	
Gypsum (powder)	25	0.043	26.
Slag	25	0.064	
Asbestos	50	0.098	36.0
Coke (powder)	50	0.110	

Building and Refrigeration Insulation.—Building insulation has become very common in the past few years. Both organic and inorganic insulators are used and the insulation is available in many forms: powder, wool, woven blankets, semirigid sheets, and rigid plates. Aluminum foil has found increasing use in these fields; it is available as thin foil, paper-backed foil, separated layers of foil, and rigid materials faced with foil. Insulation of this type is very light in weight and has low heat capacity. The insulation value of aluminum foil installations is due mainly to the air space left between successive sheets. The low emissivity of polished aluminum also decreases the radiation losses. Aluminum is used in preference to other metals because a smooth surface can be readily obtained (by rolling) and because its surface is inert to ordinary atmospheric gases and maintains its low emissivity for long periods of time. In both building and refrigeration insulation, the condensation of water vapor from air in the insulation may cause trouble, especially in refrigeration insulation. Usually some attempt is made to prevent free access of the outside air to the insulation, but it is about impossible to seal the insulation space completely. In refrigerator installations any insulation that is used should be inert to water.

Furnace Insulation.—For furnaces a very popular type of insulation is a mixture of 85 per cent of magnesia and 15 per cent of asbestos. It is available in the form of powder, brick, cylinders,

and other prepared shapes. The magnesia-asbestos mixture should not be used for temperatures exceeding 600°F. The mixture can be readily applied. When mixed with water, a paste is obtained which, after being applied, dries to a rigid covering. The outer surface of the insulation is protected with a cloth or metal cover. If metal covers are used, they should be polished and sufficiently inert to retain their smoothness under conditions of use. If a rough metal or cloth covering is used, its emissive power may be reduced by painting with aluminum paint.

A great variety of insulators are available. Among these are mineral wool, woven or loose, asbestos in the form of powder, fiber, paper, or cloth, and diatomaceous earth as powder or in suitably prepared forms. Mineral wool and asbestos should not be used at temperatures greater than 1000°F. For higher temperatures, 1600°F., diatomaceous earth is generally used; for the highest temperatures, 2500°F., calcined diatomaceous earth or some type of prepared refractory brick must be employed. If the insulation is in powder form, it should not be packed tightly as the thermal conductivity increases with increase in density. In many applications it is desirable to have the insulation in the form of a rigid solid. For these cases bricks and various other prepared shapes are available. Such prepared materials may be classified on the basis of their structure as having a continuous-solid or continuous-air structure. Bricks of the continuous-solid structure are prepared from mixtures of a powdered insulator with a finely divided combustible material such as sawdust. After shaping, the combustible material is burned out by baking the bricks at high temperatures. Bricks having the continuous-air structure are prepared by compressing the insulator powder and then sintering the particles together by baking at high temperatures. The thermal conductivities of bricks of both types decrease with decrease in the apparent density; *i.e.*, bricks with high porosity are the better insulators. In some cases the bricks not only must function as insulators but also must be resistant to high temperatures and the action of various corrosive agents, such as liquid slags, liquid metals, and gases. Materials intended for this purpose are called "refractories" and are discussed in Chap. III.

Electrical Insulators

Many different materials are in use as electrical insulating materials. The primary requisite for an electrical insulator is

low conductance. However, a large number of other factors enter into the selection of an insulator for a given purpose. The "breakdown" strength of the insulator is of great importance. For some applications the insulator must have a suitable dielectric constant; in others it must show low dielectric loss. Insulators must be inert and stable and, if solids, must have physical and mechanical properties that are suitable for the particular application.

Conductance.—The specific conductance is a direct measure of the conductivity. It may be defined as the conductance of a cube of material having a volume of 1 cc. The unit of conductance is the mho (reciprocal of ohm). Specific conductance values vary over very wide limits. For silver, the best solid conductor, the specific conductance is about 10^{29} times that of sulfur, one of the best solid insulators.

Breakdown Strength.—The breakdown strength of an insulator is the voltage required to puncture a given thickness of the insulator. It is generally given in units of kilovolts per millimeter. Unless suitable precautions are taken in the measurement to eliminate edge effect, the variation in the breakdown strength with thickness will not be linear and comparisons of specimens with unequal thickness will result in misleading values.

Dielectric Constant and Dielectric Loss.—The dielectric constant of any substance is given by the equation:

$$\epsilon_x = \frac{C_x}{C}$$

where ϵ_x is the dielectric constant, C_x is the capacity of a given condenser using the given substance as the dielectric, and C is the capacity of the same condenser using air as the dielectric. The dielectric loss is the energy loss in the dielectric when subject to an alternating field.

Chemical and Physical Properties.—All insulators must be stable and inert under conditions of use. If the insulator is in contact with the atmosphere, it must not be hygroscopic or must be suitably protected against water. In some applications, the insulator must be stable at high temperatures. The physical properties needed vary with the particular application. In some cases solid insulators are required to have great rigidity and mechanical strength; in others the insulators must be flexible.

Gaseous Insulators.—The ordinary gases such as air, nitrogen, and carbon dioxide, have very low conductivities and are excellent

insulators provided they are not exposed to ionizing radiations. The dielectric constant of most gases is close to 1 and the dielectric loss is negligible. The breakdown strength of air at 1 atm. pressure is only 30,000 volts per cm. under the most favorable conditions; this value is considerably less than for most solids and liquids. If air is used for insulation, the conductors must be widely separated for high voltage differences. For conductors that must be placed close together, it is essential to use solid and liquid dielectrics. If the solid insulator is porous, it is necessary to fill all voids with liquid or solid to avoid breakdown of the insulation at the voids.

Liquid Insulators.—Liquid insulators are used in rheostats, transformers, switches, and for the impregnation of porous solid insulators such as paper. In transformers and switches the liquid also serves as a heat transfer agent. Refined saturated paraffin oils are commonly used. Such oils must be free of water, organic acids, and other impurities. In oil-impregnated solid insulators, temperature changes result in the formation of gas pockets and ionic discharge in these pockets leads to decomposition of the oil with formation of gases and solids. No oil is completely immune to the electrical discharge but the decomposition may be reduced by adding certain aromatic compounds, such as diphenyl, to the oil. In recent years synthetic liquid dielectrics such as chlorinated aromatic compounds have been developed. Owing to their higher cost, the use of synthetic insulators is confined mainly to those installations where a noninflammable insulator is required. In impregnated paper insulation, the synthetic compounds possess an advantage over oil in that they have a higher dielectric constant and one that approaches the dielectric constant of the paper more closely. This characteristic permits the design of more compact impregnated-paper condensers than were previously possible with oil as the impregnating agent.

Solid Insulators.—Many types of solids are used for insulation purposes. They may be naturally occurring substances or entirely synthetic. Some natural insulators together with their more important characteristics are listed in Table 100.

Amber is a natural petrified resin found on the Baltic coast and in Burma. With quartz and sulphur it is one of the best insulators, ranking second only to quartz. Unlike fused quartz, the conductivity of amber is not increased by contact with small amounts of water vapor. In comparison with quartz and sulfur, it has better physical characteristics and is more inert than sulfur.

Owing to the high cost of amber (about $12 a lb.), it is used sparingly wherever excellent insulation is required as in electrometers and other sensitive electric instruments.

TABLE 100.—PROPERTIES OF NATURAL SOLID INSULATORS

Substance	Dielectric constant	Specific conductance, mhos	Breakdown voltage, kv. per mm.
Amber	2.9		
Asbestos (paper)	2.7	5×10^{-6}	4.
Maple (paraffined)	4.1	3×10^{-11}	4.5
Marble	7–9	10^{-9}–10^{-11}	2–4
Mica	7–8	10^{-15}–10^{-17}	80–200
Paraffin	1.9–3.3	10^{-16}–10^{-19}	15–50
Rubber (hard)	2–3	3×10^{-14}	10–38
Shellac	2.5–4		
Slate	6–8	10^{-8}	0.2–0.4
Soapstone	....	2×10^{-9}	1.0
Sulfur (rhombic)	3–3.8	5×10^{-24}	

Asbestos is hydrated magnesium silicate, $3MgO \cdot 2SiO_2 \cdot 2H_2O$. It is not a particularly good insulator but is valuable as an insulator because of its noncombustible nature and its great thermal stability.

Paraffin is a saturated hydrocarbon obtained as a by-product in the refining of certain types of petroleum crudes (page 95). It is an excellent insulator and is inert with respect to most reagents. Paraffin is very resistant to water and is used to prevent water absorption of hygroscopic insulators such as wood or paper. A natural paraffin found in the vicinity of certain oil fields and called "ceresin" or "ozocerite" has a higher melting point than ordinary paraffin and is a better insulator.

Marble, slate, and talc have been used primarily for switchboards. These substances are noncombustible and are easily machined. All have a tendency to absorb water and such absorption decreases the insulation. Talc on being heated to about 1100°C. becomes very hard and is marketed as "Lava" or "Isolantite." It is an excellent insulator but it cannot be machined in the hardened state. The forming of the insulator must be done before it is hardened.

Mica is one of the most widely used solid insulating materials. Many varieties of it are known, but not all of them are suitable as insulators. It is mined in the form of rough cakes which can be

split and trimmed to give thin sheets. Mica has a high breakdown strength and furnishes adequate insulation when used in very thin sheets. It may be readily split with a knife or by rolling into sheets having a thickness of only 0.0005 in. In the form of thin sheets it is very flexible. Mica has high thermal stability and is stable at 600°C. It softens around 1200°C. (2190°F.). At temperatures greater than 600°C. (1110°F.) it slowly disintegrates into scales and flakes. Mica is commonly used as a form for winding heaters such as those in electric irons. Because it can be obtained readily in very thin sheets, it finds great use wherever space for insulation is limited. "Built-up" or "reconstructed" mica is sometimes used. To prepare insulation of this type, mica flakes are mixed with a binder such as shellac and the mixture is then pressed together into a sheet, using heat and pressure. As the binder is usually organic in nature, reconstructed mica cannot be used at high temperatures.

Rubber is a very common insulator and is used either in the soft vulcanized state or in the hard state. Rubber is not only an excellent insulator but is also unaffected by moisture. In the soft vulcanized form, rubber is used as a wire covering, as an impregnant for tapes, and as a constituent of insulating paint. Hard rubber is used as any other solid insulator. It is easily machined but at room temperature slowly deforms under pressure. Like any other organic substance, it should not be used much above 100°C. (212°F.). The properties of rubber are discussed more fully in Chap. XVIII.

Gutta-percha has a high dielectric strength and is a better insulator than rubber. It is used in the insulation of submarine cables. Like rubber, gutta-percha is obtained from the sap of certain tropical trees. It is similar to rubber in many respects, but unlike rubber it is used chiefly in the natural or unvulcanized state although it can be vulcanized. Gutta-percha is plastic but is not elastic like rubber. It can be readily molded into suitable shapes by the application of pressure and heat (120°C.).

Shellac (page 572) is an excellent insulator and is impervious and inert to water. It is soluble in methyl alcohol and solutions of shellac in alcohol are frequently used for the impregnation of wood, tapes, and other solid insulators. Around 150°C. (300°F.) shellac softens and may be used as a binding agent.

The properties of a few of the more common synthetic solid insulators are given in Table 101.

TABLE 101.—PROPERTIES OF SYNTHETIC SOLID INSULATORS

Substance	Dielectric constant	Specific conductance, mhos	Breakdown voltage, kv. per mm.
Cellulose (paper)	4–7	10^{-9}	
Cellulose acetate	6–8	10^{-10}	23–28
Cellulose nitrate	4–7	10^{-10}	12–30
Fiber (vulcanized)	4–5	10^{-11}	3–18
Glass (soft)	5–8	10^{-10}–10^{-14}	230
Glass (Pyrex)	4.5	10^{-14}	134
Methacrylic resin	2.8		
Phenol formaldehyde resin	5–7.5	10^{-11}–10^{-12}	25–52
Porcelain	4.4–6	10^{-12}–10^{-15}	12–28
Quartz (fused)	4.2		
Styrene resin	3	....	20
Urea formaldehyde resin	5–6	....	12–16
Vinyl resin	4	10^{-15}	16–20

Cellulose in the form of paper is used extensively in cable construction and in many types of electrical equipment. In many cases the paper is impregnated with oil, paraffin, shellac, pitch, or varnish to prevent water absorption and to fill voids. Cellulose is a carbohydrate with the same empirical formula as starch, $C_6H_{10}O_5$, and is the main constituent of plant fiber. The chief source of cellulose is wood pulp, but cotton, flax, hemp, and cloth rags are also important sources. In the preparation of cellulose from wood, the wood pulp is treated to remove gums, resins, lignin, and other noncellulosic substances. Two processes are in common use: the sulphite process and the soda process. In the former the wood is heated with calcium bisulphite liquor for 10 hr. in a pressure vessel. The soda process uses a sodium hydroxide liquor and a heating period of about 8 hr. The sulphite process is used for spruce, fir, and other conifers; the soda process is employed for poplars, beech, and basswood. After digestion the pulp is screened and washed. It is then mixed with water and beaten to fray the edges of the fibers. In paper intended for insulation purposes no inert fillers or sizes are added. The paper sheet is formed by shaking a dilute suspension of the pulp on a moving and vibrating wire screen of fine mesh. Water is removed by suction and absorbent felts. The surface is given a smooth finish by passage through heated calender rolls.

A special type of paper, similar to parchment, is made by treating paper with a warm concentrated solution of zinc chloride in water. Under this treatment the surface of the paper becomes gelatinized due to hydrolysis of the cellulose. If, in this gelatinized state, many sheets are pressed together, the surfaces fuse together and form a homogeneous, dense mass of fiber. The zinc chloride is removed by thorough washing with water and, after drying, a hard insoluble material, called "vulcanized fiber," is formed.

Cellulose nitrate is prepared by treating cellulose with a mixture of nitric and sulfuric acid. After nitration the product must be carefully washed and stabilized. Various types of cellulose nitrate differing in nitrogen content can be prepared. The lower nitrated celluloses are soluble in various solvents and may be used for impregnation purposes. Cellulose acetate is obtained by treating cellulose with a mixture of acetic anhydride, glacial acetic acid, and sulfuric acid. Both cellulose acetate and nitrate are plastic with application of heat and pressure and may be molded into any desired shape.

Glass and *fused quartz* are excellent insulators and are inert to moisture. Neither of these substances can be machined and both must be formed at high temperatures. In the absence of water vapor, fused silica is probably the best insulator known and is used where extremely good insulation is required. Silica adsorbs water on its surface and its conductance is increased. Such adsorption may be minimized by placing a drying agent in the vicinity of the quartz or by coating the quartz with a thin layer of ceresin wax.

In recent years the organic chemist has discovered many synthetic resins. These are considered in more detail in Chap. XVII. Many of these resins are excellent insulators and find extensive use as such in spite of their relatively high cost.

The *phenol formaldehyde resins*, commonly called "Bakelite," are used extensively for insulation purposes. Bakelite may be obtained as the pure transparent resin, as a molded resin with wood flour, fabric, asbestos fiber, or mica flakes as filler, or as a laminated resin with paper or fabric filler. Once formed, Bakelite is stable indefinitely at 120°C. (250°F.) and does not soften. It is inert and shows low absorption of water. It possesses high tensile strength and may be machined.

Other types of synthetic resins are in use. "Victron" is a resin prepared from styrene, has low dielectric loss, and is used in radio sets. "Vinylite" is prepared from vinyl chloride. "Lucite" is a

methacrylate resin. Urea formaldehyde resins are called "Beetleware" or "Plaskon."

The use of *ceramic insulation* is very common. Many different varieties of porcelain are in use. Porcelain is prepared by mixing China clay, ball clay, feldspar, and ground quartz with water and working the mixture until a plastic mass is obtained. The mix may be pressed into the desired shape and dried. After drying it is heated or "fired" to a high temperature which fuses the feldspar and binds all the constituents into a hard, dense vitreous mass. The temperature used controls the porosity and the nature of the product. High temperatures (1285°C.) produce a more vitreous and a less porous ware. Porcelain for high-voltage insulation is usually high-temperature porcelain.

A special hard porcelain, low in feldspar, is used for spark plugs where a high dielectric strength at high temperatures is required together with great mechanical strength and great resistance to thermal shock. Spark-plug porcelain is fired around 1465°C. (2670°F.), has no porosity, and is similar to the porcelain used in chemical laboratory equipment.

For resistance units such as those in furnaces, heaters, and flatirons, hard porcelain of the spark-plug type may be used. However, special porcelains, called "Lava," made from soapstone or periclase, MgO, are used. Such insulators must withstand high temperatures but only low voltages. For this reason they do not need to be completely vitreous; in fact, their resistance to thermal shock is improved if they are not vitrified.

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